AMERICAN DYESTUFF REPORTER

"Circulated Everywhere Dyestuffs Are Used"

Published by Howes Publishing Company, 440 Fourth Avenue, New York

Devoted to the practical application of dyestuffs in all industries; especially to textile chemistry—the science and practice of scouring, bleaching, dyeing and finishing.

VOLUME XXI | AUGUST 29, 1932 | NUMBER 18

Some Aspects of the Structure and Properties of the Rayons*

By HAROLD DE WITT SMITH

The Society in its tentative specifications for tolerances and test methods for rayon has defined rayon and the several commercial types of rayon and has provided to all who are concerned with the manufacture and use of this material an acceptable guide to test procedure and allowable tolerances. In the drawing up and in the revision of such a specification as well as in the technology of rayon manufacture and use, that knowledge of the material and its properties whose promotion is one of the objects of the Society is essential. The knowledge of the internal structure of the rayons has made great strides in recent years.

All of the present-day rayons are made from cellulose. In three of the four commercially successful processes the finished product is highly purified cellulose, the fourth type is a derivative of cellulose. Cellulose is a carbohydrate with three available alcoholic hydroxyl groups. Chemical and physical research have indicated that it has no definite molecular weight. It is built up from ring-shaped glucose residues joined to one another by oxygen bridge to form long chains or "thread molecules." These are grouped parallel to one another into long slim bundles or micellae, these micellae into larger bundles and so on up to the physical boundaries of the visible fibers of cotton, wood or other native cellulosic material. In the manufacture of rayon this orderly structure is broken down and the coagulated filament is composed of a more or less heterogeneous matted mass of micellae and micellar fragments. The degree of orientation of these particles can be controlled to a considerable extent by the method of spinning.

As a result of this micellar structure the degree to which these rod-like particles are oriented within the rayon filament is an index to its behavior. Since the strength of such a structure depends upon the mutual cohesion between the micellae and this in turn upon the area of mutual contact between them, increasing orientation increases the strength. This is accomplished however, at a sacrifice of the elongation. The plastic flow exhibited by all rayons under constant loads is brought to a halt by the increasing intermicellar attraction as the orientation of the flowing micellae improves. The "relaxation" of rayon filaments at a constant extension also alters the orientation and hence the rigidity of the filament.

Cellulose is a very hygroscopic material. The behavior of rayon is very sensitive to changes in amount of absorbed moisture. The absorbed moisture pries the micellae farther apart and acts as an internal lubricant. Hence the cohesive forces are decreased and the deformations and orientations due to the application of external forces proceed more readily.

Attention is also called to the effect of the micellar structure and of the swelling due to moisture absorption on the behavior of the rayons with respect to chemicals and dyes.

THE Subcommittee on Rayon of the Society's Committee D-13 on Textile Materials first undertook the preparation of a specification for tolerances and test methods for rayon in 1926. This specification is still continued as tentative because of the need for revision from time to time occasioned by the actively developing rayon industry. It provided the first published standard in this country, if not in the world, for a general testing procedure acceptable to both producers and consumers of rayon and for tolerances for some of the physical properties of this material. The specification is in four parts —definitions, identification, tolerances, and test methods.

The aim of this paper is briefly to review the types of rayon as defined in the Society's rayon specifications and then to offer a concise survey of the knowledge of their internal structure, which would-wide research has recently provided, and to examine the relationship of this structure to some of the properties and characteristics which must be considered in drawing up and in revising rayon specifications as well as in the successful utilization of rayon in the textile mill.

What Is Rayon?

The Federal Trade Commission adopted the word "rayon" to replace the words "artificial silk." This Society has defined rayon as follows: "A generic term for filaments made from various solutions of modified cellulose by pressing or drawing the cellulose solution through an orifice and solidifying it in the form of a filament or filaments by means of some precipitating medium."

This definition embodies the fundamental fact that all of the present commercial methods of producing rayon utilize cellulose as the raw

*Presented at Annual Meeting A. S. T. M.

material. The rayon industry is still wholly a cellulose industry despite constant efforts to manufacture filaments from other raw materials such as silk waste, gelatine, chitin and other substances.

Historically, the birth of the rayon idea appears to have been the suggestion by Robert Hooke, in 1665, of "the possibility of spinning a Kind of Artificial Silk out of some glutinous substance that may equal Natural Silk."

After some two hundred years of rather primitive and desulatory efforts by various investigators to imitate the silk worm, Count Chardonnet, who had made a careful study of sericulture in China, and Japan, achieved, in 1884, a failure which was really a success. He digested mulberry leaves in nitric acid and succeeded in spinning a solution of the resultant mass in organic solvents into silk-like filaments. But although they were nitrogenous, they were chemically quite unlike silk, which is a protein or animal substance. They were in fact a derivative of cellulose and hence chemically more like vegetable than like animal fibers. Realizing this, he turned, naturally, to cotton, a cheaper and better source of cellulose than mulberry leaves. By 1890 he had learned how to denitrate his filaments, thus reducing their inflammability and improving their textile and dyeing properties.

During the next fifteen years other methods of getting cellulose into solution were developed and out of this pioneering work have grown the four present commercial processes whose nature is indicated by the following definitions from the Society's rayon specification.

"Nitro-Cellulose Rayon (Chardonnet). — Filaments composed of a regenerated or denitrated cellulose which has been coagulated or solidified from a solution of nitrated cellulose." The nitrated cotton is dissolved in an ether-alcohol mixture and extruded through fine holes into warm air. The resulting filaments, after subsequent denitration, are composed of cellulose in a very pure form.

"Viscose Rayon.—Filaments composed of a regenerated cellulose which has been coagulated or solidified from a solution of cellulose xanthate." The xanthate is produced by treating mercerized cotton or wood pulp with carbon bisulfide. It is soluble in water and is extruded into an acid bath which coagulates the filaments. Subsequent treatment includes desulfurizing, bleaching and washing. The resulting filaments are composed of pure regenerated cellulose.

"Cuprammonium Rayon.—Filaments composed of a regenerated cellulose which has been coagulated or solidified from a solution of cellulose in ammoniacal copper oxide." This solvent disperses cellulose directly to an aqueous solution. It may be spun into water or into acid or alkaline baths and is particularly amenable to stretching while in a semiplastic state, with effects to be discussed later.

"Cellulose Acetate Rayon.—Filaments composed of an acetic ester of cellulose which has been coagulated or solidified from its solution." The ester is made by treating cotton with acetic anhydride dissolved in acetic acid in the presence of a catalyzer such as sulfuric acid. By subsequent partial hydrolysis, a cellulose acetate is obtained which is soluble in acetone. This solution is spun into warm air and the resulting filaments of cellulose acetate are ready for use, except for subsequent textile processing such as twisting and winding.

The difficulty of identifying with certainty the type of a given sample of rayon is evident from the fact that three of the four types consist in their finished state of a very pure form of cellulose. Identification of the cellulose acetate type is of course simple because its chemical behavior is distinctive from the others. The scheme of identification of the three others, adopted in the rayon specification, depends upon the presence of minute amounts of impurities which are characteristic of the manufacturing process, for instance, nitrogen in the case of the nitrocellulose type and sulfur in the case of the viscose type. Because of improvements in the manufacturing processes, however, and the consequent reduction of these residual impurities, the reliability of such methods may be affected. Hence, the necessity of revision of the standards from time to time to meet the new conditions by embodying the best of such new methods as are worked out by the members of the Society and by other interested bodies who are working along similar lines.

The Structure of Rayon Filaments

Included in the avowed purpose of the Society, namely, "The promotion of knowledge of the materials of engineering and the standardization of specifications and the methods of testing," is the obvious but vital realization that sound standards and specifications must be based on a fundamental understanding of the nature and structure of the material in question.

Here then is a summary, or better, a "synthesis" of some of that "knowledge of the material" which persistent, world-wide research on cellulose in general and on rayon in particular has provided for the benefit of all to whom, like the rayon subcommittee, it may be of interest and of importance.

Structure of Native Cellulose:

Ultimate analysis of purified cellulose indicates the presence of carbon, hydrogen, and oxygen in the ratio $C_6H_{10}O_5$. Chemical research has yielded among many interesting facts, three which have been very helpful in revealing its structure. (1) it is a carbohydrate and can be broken down by hydrolysis (the addition of hydrogen and oxygen in the proportion in which they are present in water) to a sugar, glucose ($C_6H_{12}O_6$) whose yield under proper conditions of hydrolysis is practically quantitative; (2) it has three available hydroxyl groups per $C_6H_{10}O_5$ and consequently behaves like an alcohol with respect to many acids, forming esters as high as the triester with acids, such as the nitrate, acetate and in fact a greater number of organic acids; (3) these three hydroxyl groups are attached to particular carbon atoms, namely, the second, third and sixth when numbered according to the order usually employed in writing the

structural formula. By repeated methylation followed by hydrolysis, a quantitative yield of 2-3-6 trimethyl glucose can be obtained.

Chemical research on glucose has resulted in the acceptance of a structural formula for one form, known as beta-glucose, in which five of the carbon atoms and one oxygen form a six-atom ring to which the remaining atoms in the glucose molecule are attached as branches. By the removal of the equivalent of one molecule of water, namely, one hydrogen atom from one side of this ring and one hydroxyl group from the other side, these glucose residues may be joined by the chemical bonds of the oxygen bridges between them to form long chain structures. Each succeeding glucose ring in the chain is rotated through 80 deg. about the chain axis so that alternate rings are "face up" and those between them "face down."

Physical research on cellulose fibers, principally by means of X-ray diffraction photographs, confirms this structure. In addition to revealing that the atoms and atomic groups in cellulose are arranged with such regularity that the internal structure of the fibers is decidedly crystalline, this modern research tool has provided accurate information as to the distances between atoms in various configurations, such as C-C, C = O, C-O and O-H.

The combination of these crystallographic dimensional data, the space relationships and dimensions of the cellulose unit cell as revealed by the X-ray, and the known chemical behavior has confirmed this chain structure as outlined above as the one which best fits the properties and behavior of cellulose. Figure 1 gives the empirical and the structural formulas of glucose and cellulose as well as sketches of the space models which visualize the atomic configuration much more clearly than any word description. The large spheres are carbon; the medium spheres, oxygen; and the small spheres hydrogen atoms.

Cellobiose, which appears in the figure, is an intermediate product in the hydrolysis of cellulose to glucose. It does not occur in Nature. It is included because it is so frequently mentioned in the literature on cellulose structure. Hydrolysis readily breaks down the cellulose into cellobiose and finally glucose. The synthesis of glucose into cellulose, however, has remained until recently an exclusive process of Nature accomplished in the green parts of living plants under the influence of sunlight. In fact, Nature starts with carbon dioxide gas and water and builds these up into glucose, starch and cellulose. An account of the synthesis of glucose from carbon dioxide and water by an English chemist has recently failed of confirmation by others who have attempted to duplicate his reported results by following his directions.

A recent announcement from McGill University of the synthesis of cellulose membranes from glucose by means of enzymes, however, may be the first step in wresting from Nature one more of her secrets. Nevertheless, for the present, and one may safely say for a considerable future, rayon will be made from the bountiful store of natural cellulose and not from gas and water as some of our over-optimistic newspaper friends announced in headlines at the time.

The X-ray diffraction diagrams tell us more. These long chains, comprising in native cellulose some 100 to 120 glucose residues, cling together parallel to one another in bundles of some 50 to 60 chains. These bundles are called micellae, and the above dimensions are, of course, averages. Individual micellae undoubtedly vary greatly in size. The important fact is, however, that they are submicroscopic, long, rod-like particles whose lengths (500 to 600 Angstrom units[1]) are about ten times their diameters.

In the native fibers, these micellae are packed in parallel

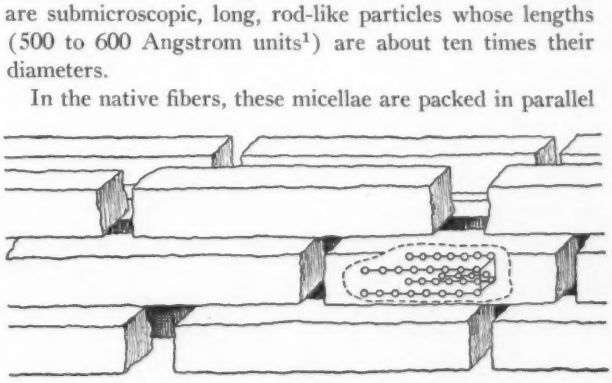


Figure 2

to one another somewhat like the bricks in a wall, as illustrated diagrammatically in Fig. 2. This of course is schematic and is undoubtedly far more symmetrical and uniform than the most perfect structure found in Nature. In fact it appears that what was formerly considered an amorphous phase or an adhesive material between the oriented micellae, is actually simply a part of the micellae which are less oriented than the ones which give the crystalline points in the X-ray diagrams. In one micella in the figure the individual glucose residues and chains are indicated.

In ramie, the micellae lie straight with their long axes parallel to one another and

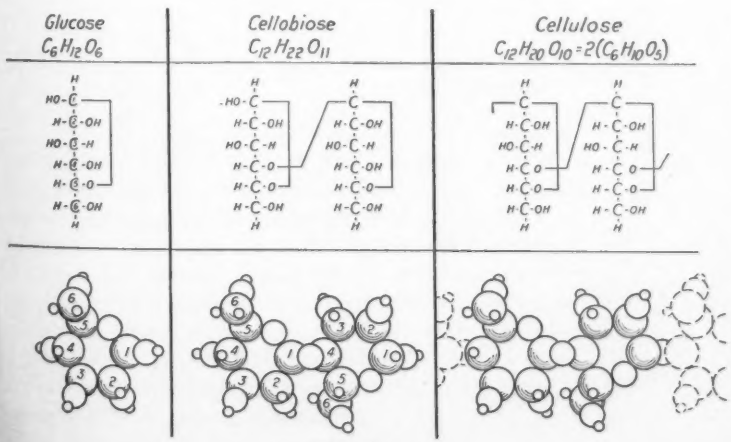


Figure 1

[1]One Angstrom unit equals 0.0000001 mm.

to the fiber axis. In cotton and wood cellulose, the long axes of the micellae are parallel to one another but they spiral about the fiber axis in concentric layers, one layer to the right, the next layer to the left. This gives a greater flexibility to the structure which is reflected in the comparative properties of the respective fibers.

Ultramicroscopic and microscopic examination of natural cellulose fibers indicates that this principle of long slim particles or bundles is repeated again and again in building up the fiber. Such names as supermicellae, fibrillae and striae have been applied to the observed elements of increasing size of which the native fibers are composed. Not only cellulose but all of the fibrous structures found in Nature including all of the textile fibers appear to be built up in this manner of bundles of long units, rather well oriented with respect to one another, these bundles forming larger bundles also in orderly arrangement, and these again forming large bundles until we have reached the physical boundaries of the visible fiber itself, be it cotton or wood cellulose or other fibrous substance.

Spinning Solutions:

What happens now when we disperse this neat cellulose structure by preparing a spinning solution for rayon manufacture? No matter which process we use, the bundles are split apart and reduced in size down to colloidal dimensions. Because the primary chemical bonds holding the glucose residues together in a chain are relatively strong, the splitting up seems to be chiefly longitudinal and results in a heterogeneous mass of micellae and micellae fragments dispersed with little or no orientation throughout the solvent medium. Actual measurements of particle size have indicated the presence of particles as fine as single chains. Much of the technique of dispersion and aging of the material during the manufacture of rayon is of course concerned with the control of the size and uniformity of the cellulose particles.

Rayon Structure:

When the spinning solution, or "dope" as it is commonly called, is forced through the fine holes in the spinnerette into the coagulating medium a considerable amount of "recrystallization" or reformation into micellae occurs. The arrangement of the micellae in the newly formed rayon filaments depends largely on the method of spinning. At one extreme is the old method of spinning the viscose type with little or no stretch; that is, the filaments are drawn off at a speed which is only slightly greater than the speed of extrusion from the spinnerette. In such a rayon, the X-ray reveals that the micellae lie in a matted mass like the criss-cross arrangement of fibers in a felt. This is schematically represented in Fig. 3.

At the other extreme is the stretch spinning of Lilienfeld viscose yarn or of the cuprammonium yarns in which the filaments, while still in a partially coagulated state, are subjected to considerable draft or stretching by reeling them up much more rapidly than they are extruded. The effect of this stretching of the plastic mass is to pull the micellae into line in the direction of the filament axis with consequent increased orientation, as indicated in Fig. 4.

No matter what the process of dispersion or the method of spinning, the final structure of the rayon filament thus resembles that of the native fibers in that it is composed of a mass of long slim particles or micellae, but differs from the natural fibers in that the micellae are smaller and less regular in size and form a more imperfectly arranged network. Most of the differences between the properties of natural fibers and of rayons as well as the distinctive behaviors of the several types of rayon are intimately connected with the orientation of the micellar structure.

The Relation Between Micellar Structure and Properties of the Rayons

Effect of Orientation on Strength and Elongation:

While the exact nature of, and differences between the several forces holding together the elements of such a structure are not too clearly understood as yet, it is quite certain that of the three bonds, namely, the longitudinal bonds between the glucose residues in a chain, the lateral bond between the chains in a micella and the lateral bond between the micellae, the latter is the weakest. Hence the strength of a cellulosic fiber or filament is determined by the strength of the inter-micellar attraction and this in turn is proportional to the area of mutual contact between micellae. This explains one

Table I.—Relation of Orientation to Strength According to Clark

Type of Rayon	Orientation	Strength, G. per Denier
Ordinary viscose	Moderate	1.51
Viscose sewing rayon	Very good	2.69
New viscose rayon	Very good	2.74
New viscose rayon	Very good	3.77
Lilienfeld	Excellent	4.12
Real Silk	Excellent	2.94

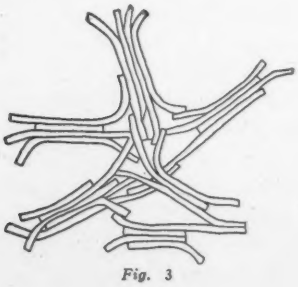


Fig. 3

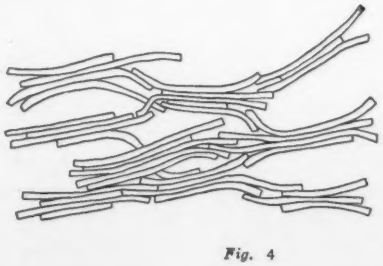


Fig. 4

of the fundamental precepts in the art of spinning rayon, namely, that while we can control the spinning of any given type with respect to either strength or elongation, we cannot control both of these factors arbitrarily beyond certain narrow limits. The more perfect the orientation of the micellae the greater is the strength because of the increased area of contact between them, but the lower is the elongation because the "slack" due to the criss-cross orientation has already been taken up.

The relationship between orientation and strength is indicated by Table I which was compiled by Clark. It should be noted, however, strength alone is no criterion of excellence. It is in fact quite possible for a rayon to be too strong to be good for textile purposes because of concurrent insufficient elongation. The excellence of a rayon, as of any textile yarn, is determined by the perfection of the balance between strength, elongation and other characteristics, and this proper relationship between the several properties is far more important than the absolute value of any one. At this point it should also be made clear that the degree of orientation is of itself in no sense an index of quality, it is merely an index of behavior because of the fact that the internal structure is micellar in nature.

Effect of Orientation on Plastic Flow:

Within the range of small elongations, rayon filaments are truly elastic and obey Hooke's law when loaded and unloaded rapidly. If a small load be hung on a rayon filament or yarn, however, it causes first an immediate extension proportionate to the load, but this is followed by a further increase in length under the constant load at an ever decreasing rate until the rayon finally attains equilibrium again. Thus, while it exhibits a plasticity which is somewhat analogous to viscose flow, it differs from an ideal plastic body which would continue to flow under a constant load at a constant rate to the point of rupture. This hardening effect which rayon exhibits is undoubtedly due to the fact that the micellae tend to become more oriented by the flow or stretching of the filament and the consequent increasing mutual attraction between them acts as a brake which finally counter-balances the load and so brings the flow to a halt. When the load is removed, the filament makes an immediate partial recovery and then creeps back slowly toward its original length which it will eventually reach provided the elastic limit has not been exceeded.

"Relaxation" and Rigidity:

A corollary of this phenomenon which is called "elastic after-effect," and is present in metals also to a lesser degree, is an equally important effect known as "relaxation." If a filament be subjected to a small extension and held at exactly this extension, the internal stress set up will gradually diminish with time. There is apparently a change in the internal structure in the direction of better orientation and such a fiber will not recover its original length until immersed in water which swells it and restores the original orientation.

This phenomenon is of profound practical import in fabric manufacture because it is directly connected with many cases of shiners and streaks in warp or filling. The change in orientation, due to relaxation, even at small extensions causes a change in the rigidity of the filament and hence a yarn which has been stretched slightly and held in this stretched condition will bend or crimp differently than its neighbors in the formation of the weave and hence cause a difference in light reflection which appears as a shiner or a streak. This may not show up until the fabric has been finished since, when wetted out, the "relaxed" yarn will contract more than its neighbors, thus intensifying the difference in crimp.

Increasing orientation and increasing rigidity go hand in hand for a given filament size, but the increased fineness of filament attainable by stretch spinning offsets this factor and tends to maintain the flexibility of the yarn.

TABLE II.—MOISTURE ABSORPTION OF CELLULOSIC MATERIALS IN SATURATED AIR ACCORDING TO SHEPPARD AND NEWSOME

Type of Cellulose	Percentage Regain at 30° C. and 100 per cent Relative Humidity
Cotton linters	15.0
Hydrocellulose (acid treatment)	10.4
Standard cellulose (A.S.T.M. procedure)	17.5
Hydrated cellulose "A" (cotton mercerized without tension)	22.7
Hydrated cellulose "B" (regenerated from cuprammonium solution) (cuprammonium rayon)	23.5
Hydrated cellulose "C" (regenerated from cellulose acetate) (saponified acetate rayon)	26.6
Cellulose triacetate (completely acetylated)	8.3
Cellulose acetate film base (partially acetylated) (acetate rayon)	15.0
Cellulose nitrate (10.8 per cent nitrogen content)	5.0
Cellobiose octacetate (completely acetylated)	1.0
Glucose pentacetate (completely acetylated)	0.8

Yield Point:

An autographic record of the stress-strain relationship of a rayon yarn will show for most yarns a definite yield point at about one-half the breaking load. At this point the yarn flows rapidly under little or no increase in load. Beyond it the load-elongation proportionality is resumed again but at a different slope than in the early part of the curve. The location of this yield point and the ulti-

mate values of strength and perhaps elongation also are affected by the speed of testing because of the flow and after-effect phenomena described above. Thus the micellar structure is responsible for the need which the rayon specification has met, of specifying an exact procedure for the testing of strength in order that the results of various laboratories may check one another. The determination of elongation should be included in the next revision of this specification.

The Nature of Moisture Absorption:

Cellulose is a very hygroscopic material, being sensitive to the moisture in the atmosphere, especially when in the form of fine fibers or filaments which have a large exposed surface per unit weight. At a given relative humidity the amount of moisture absorbed depends upon the form of the cellulose or cellulose derivative.

Table II gives the moisture absorbed (as a percentage of the dry weight) at 100 per cent relative humidity for a number of materials as determined by Sheppard and Newsome of the Kodak research laboratories. Two facts stand out: First, the amount of moisture absorbed decreases as the orientation of the micellae is increased. Second, the moisture absorption decreases as the hydroxyl groups are replaced chemically by acid radicals. Both of these observations indicate that the water molecules must be attracted and held by the residual forces of the hydroxyl groups along the exposed sides of the micellae. By better orientation or by chemical replacement the number of free OH groups which can attract water is reduced.

The fact that even the completely acetylated triacetate shows considerable absorption indicates that a second factor is also operative in this case, but not in the case of the completely acetylated cellobiose or glucose. This factor is apparently the capillary action of the pores in the micellar network. This capillary effect accounts for the well-known hysteresis observed in connection with the absorption and desorption curves of the moisture content--humidity relationship. Filaments which approach equilibrium with a given humidity from the wet side show a greater regain than when they approach equilibrium with the same humidity from the dry side. This is apparently due to a locking in of the water molecules which have entered the pores as the pore spaces at the surface contract during drying.

The Effects of Absorbed Moisture:

The tremendous influence of this moisture absorption or swelling phenomenon on the properties of rayon are explainable in the light of the micellar structure. The absorbed moisture pries the micellae farther apart and so reduces the mutual attractive forces. It acts at the same time as an internal lubricant enabling them to slide and shift on one another more easily. Consequently the strength of the wet filament is lower and the elongation higher than that of the dry. Because of the sensitivity of air-dry tests to changes in humidity a definite humidity for preparing and testing rayon is specified. Because of the difficulty of maintaining accurate humidity control, most rayon plants and many consumers control their quality by wet tests whose incorporation in the rayon specification is now under consideration. Within the limits of relative humidity occurring in practice, the moisture content, and hence the strength of rayon, increases almost linearly with increasing humidity. Changes in humidity affect the properties of acetate rayon only about half as much as those of the other types because its moisture absorption is about half that of the others.

The increased internal lubrication due to the presence of moisture greatly increases the plasticity. This affects not only the ease with which rayon flows or elongates under load, but also the rigidity of the filaments. For this reason a certain degree of humidity is very desirable in textile processing. The adverse effect upon strength and plasticity is more than offset by the improvement in limberness or pliability which facilitates the formation of perfect interlacing in weaving and perfect stitch formation in knitting. Although various softening oils are used in this connection, nothing takes the place of moisture in penetrating and softening the structure of cellulose.

Another paper could be written on the relation between micellar structure and the chemical and dyeing properties of the rayons. Suffice it to say that the regenerated rayons as a group, being more open in structure than the native cellulose fibers, are more sensitive to chemical action and to dyes. Yarn which is held during dyeing under sufficient tension to stretch it, comes out lighter than unstretched yarn dyed in the same bath. Apparently the improved orientation of the stretched yarn has reduced the attraction for dyestuff probably by closing some of the pores as well as by the reduction of the free hydroxyl groups.

If it were not for the swelling of the cellulose structure in water, dye penetration would be impossible. For example, dyes which will dye rayon from a water solution will not dye it from a solution in an organic solvent which has no swelling action.

The acetate rayons are impervious to most direct cotton and rayon colors. This is no doubt due in part to the reduced swelling in water and in part to the replacement of OH groups by acetyl groups. A complete range of special acetate dyestuffs has been developed however. Most of these dissolve in or diffuse through the cellulose acetate in accordance with the laws of true solutions. They form, in fact, solid solutions in the acetate filaments.

While this review of the present knowledge of the structure of the rayons by no means exhausts the subject, it does indicate how research on cellulose is providing that knowledge of the material rayon, which is of value to the Society in its work and to all others who are concerned with its behavior and its utilization.

Testing the Quality of Waterproofed Textile Fabrics*

By E. ROLFE

A large number of methods have been devised for testing the water-resistant quality of proofed materials. These tests refer to shower-proofings, not to rubber proofings, oil-skins, or similar fabrics, which, unless they contain pinholes or are badly made up and leak at the seams, are absolutely impermeable to air and moisture. No single test, however elaborate, makes it possible to estimate accurately the resistance of a proofed fabric to weather and wear.

THE usual methods of testing ignore friction and rubbing, and consists of arrangements whereby water pressure in some form is applied to the fabric. They may be classified as follows:—

(1) Tests in which the material is made into a bag into which water is poured, to give a certain head of water pressure. Sometimes the fabric is folded into a funnel with a piece of filter paper outside.

(2) Tests in which drops of water, imitating rain, and controlled in some manner, are allowed to fall on to the fabric until penetration takes place.

(3) Tests in which the fabric is made to close the end of a glass cylinder, which is then filled with water thus applying a certain pressure. Either the rate of leakage or the pressure at which leakage first occurs is taken as the measure of waterproofness.

These three types of tests may be described as "bag" tests, "spray" tests and "pressure" tests.

A test of the first kind is sometimes used as a shop-window advertisement. The fabric to be demonstrated is made to form the bottom of a shallow tray, which is filled with water to the depth of about one inch. The water is sometimes caused to flow, maintaining an unaltered depth, or otherwise the tray is agitated. The display looks impressive, but any moderately proofed cloth will stand this treatment for an indefinite time, as the efficacy of a test depends on the head of water applied, which is small in this arrangement.

The usual way of conducting a "bag" test is to support a piece of fabric by its corners so that a bag is formed, into which water is poured until a maximum depth of four inches is attained. No leakage should occur after 24 hours.

Crumpling and Soaking

The same test may be carried out less crudely by use of a large glass filter-funnel. A piece of fabric 12 inches square is cut, crumpled thoroughly in distilled water and left to soak. Every hour the test piece is taken out, straightened, recrumpled and again left to soak. After six hours immersion it is taken out, straightened, dried and allowed to condition for 24 hours. This treatment is designed to break up the proof and remove any soluble constitutents, thus to some extent imitating the conditions of wear. The material is then folded within a similar square of filter paper, and fitted into the funnel. 500 c.c. of water are poured in and if the proof is first class the filter paper on the outer side of the sample will not be wet after 24 hours. A degree of comparison between fabrics may be obtained by measuring the volume of water which percolates through after certain intervals of time.

"Spray" Tests

Before proceeding to describe more elaborate tests, it must be admitted that no laboratory experiments can estimate the resistance of a proofing to weathering by which is meant alternate wetting and drying, combined with rubbing and rough treatment. Thus, tests can only be made on fabrics when new, although some effort, such as has been described, may be made to break down the film of proofing substance, as this deterioration takes place very quickly in wear. Some proofings show excellent water-resistance when quite new and undisturbed, but consisting as they do of a surface film of brittle and easily removed substances, they very quickly lose quality in wear.

"Spray" tests vary from the device of giving a garment, placed on a model and sealed at the neck, a healthy showerbath, to the accurately controlled War Office Drop Test. Anyone handling proofed goods may assemble some sort of spray test which will give a rough idea of whether goods supplied are up to standard. The difficulty lies in attaining regularity of water pressure from the spray.

The Drop Test is probably the best known of all methods of testing waterproofness, but it is very difficult to carry out successfully with the resources of the average works laboratory. The test sample is clipped over a piece of filter paper on to a glass plate, which is supported at an angle of 45 degrees.

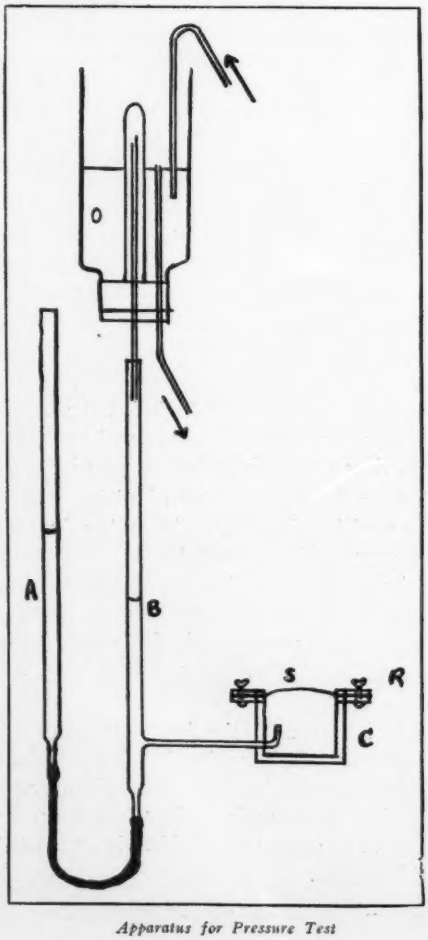
*Dyer and Calico Printer.

Accurate Control of Drops

Under the glass plate lies a mirror in which the observer may see an image of the filter paper which lies between the test piece and the glass supporting plate. An arrangement is made by which drops of water are allowed to fall exactly six feet on to the test piece, at a rate of 18 drops per minute. Observation is made of the number of drops required before penetration of the fabric causes a wet stain to appear on the filter paper. The great difficulty with this test is that vibration tends to cause the falling drops to go astray, so that they do not all fall exactly on the same spot, and draughts have the same disturbing effect. The latter may be eliminated by means of a long glass cylinder which protects the drops as they fall, but the vibration factor is not easily overcome. Objections have also been raised on the ground that this test is not accurate in that it deals only with a small area of fabric surrounded by a large dry area. Some of the largest testing houses use this test and when carefully arranged and carried out it seems quite reliable.

Apparatus for Pressure Test

The following test of the "pressure" type is more easily carried out, and the apparatus can be erected by anyone willing to take a little trouble. A small brass vessel must be made, consisting of a cylinder C, about 5 centimetres deep, with a side inlet at its base and a turned flange at the top, containing screw holes. An accurately fitting brass ring R screws down on to the cylinder so that the test piece S can be tightly stretched across its mouth. The aperture has a diameter of about 5 centimetres. Water is delivered into the cylinder from the burette B with side tube. Connection is made with an auxiliary burette A by means of which the cylinder may be filled rapidly at the beginning of each experiment. An arrangement for maintaining a constant level in an inverted bottle O is erected, and the head of water in the burette B is increased at a constant rate by allowing the water to run in through a capillary of selected diameter. Water is run in at the rate of about 0.5 c.c. per minute. The zero reading is that level of water in the burette B when the pressure of water in the cylinder causes the test piece to bulge slightly. The head of water is allowed to increase until the first drop becomes visible on the surface of the test piece. The slower the rate of increase of the head of water the more accurately discriminative is the test, but at the rate indicated above a considerable time is required for each test.



Apparatus for Pressure Test

Modifications of this arrangement, in which the volume of water which percolates in a given length of time under a fixed head of water pressure is measured, are not so reliable. In such tests the fibers become soaked and swollen, the woven structure is distended, and the conditions are clearly abnormal.

Innumerable ingenious devices have been tried which aim at taking into account friction, as for example, where a head of water is applied while the fabric is gently stroked by a mechanical arrangement, on its underside.

So wide is the range of materials which are given waterproofing treatment that it is impracticable to attempt to discuss figures showing what results represent good proofing. The uses to which the materials are put varies greatly also. Some fabrics used to-day for advertised waterproof garments were found to be penetrated at the first drop by the Drop Test described. The material made up in double thickness gave a waterproofing effect, satisfactory for its purpose, for even when the outer ply of fabric was soaked, the lining resisted the wet well. Other materials stand 60, 70 and even 100 drops.

In order to obtain a fabric which will stand 60 or 70 drops, or withstand a head of 20 to 25 c.c. of water without leaking, it is necessary that the unproofed material should have a certain density of structure, which is estimated by air porosity determinations. This further investigation is outside the scope of those for whom this article is primarily intended, but a description, with a long list of results obtained on different materials by the water pressure method, may be found in the Second Report of the Fabrics Co-ordinating Research Committee (H. M. Stationery Office).

Anomalies and Defects of Color Vision*

Tests for Color Blindness*

By Dr. MARY COLLINS, M.A., B.Ed., Ph.D.

ABOUT 1797, Dalton, the great chemist, made the discovery that he was color-blind and published a very accurate and detailed account of his own color vision. This was really the beginning of a systematic study of color-blindness, for with Harris' case the nature of the defect was not realized.

It is not so very long ago that color blindness was "discovered." The earliest case on record belongs to the end of the eighteenth century, about the year 1777. A shoemaker, Harris by name, found he had considerable difficulty in distinguishing certain colors, and when this became known there were many journeyings to and fro all over the country to see this strange person. His first suspicions were aroused when he was about four years old. Having found a stocking in the street, he carried it to a neighboring house to enquire for the owner. He observed the people called it a red stocking, though he did not understand why, as he thought it completely described by being called a stocking. He observed also, when young, that he was unable to distinguish cherries from their leaves except by shape. This first account appears to be a description of blindness to both red and green.

At the present day, there are said to exist three varieties of color-blindness. The first type is that of total colorblindness or achromatopia. It is not of frequent occurrence, only about eighty cases having been described up to date. To the totally color-blind, the spectrum is a colorless band, differing only in luminosity. Red may appear black; orange, dark grey; yellow, light grey; and so on, the other colors varying only in shades of grey. It is difficult to imagine the visual sensations of an achromatopic subject, but we may roughly compare his world to that of an engraving, in contradistinction to a corresponding colored picture.

A second variety of color-blindness which has been found is that of blue-yellow blindness, where ability to see blue and yellow is affected, but ability to see red and green quite unaffected. Generally it is accompanied by some pathological change in the eye. One case, reported by Miss Richardson, saw blue as a dazzling white, and on being asked to describe the color of the costume Miss Richardson was wearing, seemed much embarrassed. For the navy blue costume, as he admitted afterwards, appeared to him as white with all the stains and grease marks clearly shown!

The third form of color-blindness, red-green blindness is the most important of all because of the frequency with which it occurs and because of the colors which are confused, since they are used for signalling purposes. It becomes increasingly important when it is realized that the existence of the defect in the male population has been estimated at four per cent. With women, only about one in 500 suffers from this disability. Unfortunately too, this defect is congenital and hereditary, and no cure is possible. Although color-blindness may exist on the male side of a family it will be found to be practically non-existent on the female side. A female, however, whose father is color-blind, may transmit the defect to her sons.

Color-blindness must not be confused with color ignorance. The latter can, of course, be cured, for it is only a matter of learning the names for the colors and associating them properly. Color-blindness is totally different. No matter how hard one tries to teach the names of color to a color-blind person, the efforts will be fruitless. The defect consists in a distinct inability to perceive certain colors. As far as a color-blind is concerned, there are certain colors which are non-existent and to which he is blind. Otherwise, his vision is normal.

A Reproduction System

It has been more or less agreed that color-blindness is a reproduction system of normal color vision. The color-blinds lack something which the normal eye has, but have nothing which the normal eye does not possess. The person with normal color-vision sees a spectrum of six or seven colors. The red-green color-blind has a spectrum of only two colors—blue and yellow.

An investigation by the Psychology Department at Edinburgh University into the color experiences of red-green color-blinds seemed to show conclusively that their color sensations were indeed yellow and blue, but the extent to which these two colors replace all other colors in the spectrum is not constant for every color-blind. With some, yellow and blue may replace all the other colors. Red, orange, yellow and green may be seen as different shades of yellow; blue and violet as different shades of blue. The red will be a very dark yellow and will appear in fact, almost black with just a tinge of yellow in it. The orange will not be quite so dark, the yellow will be brighter, and so on.

It will be evident that under such circumstances a person may be quite unaware of his defect and others may be unaware of its existence. By convention, the color-

*Part of a paper read before the Royal Society of Arts, Edinburgh.

blind has learned that what he sees as a black with a tinge of yellow is called red by other people and he naturally associates this particular shade of yellow with the name of red. Similarly, a very dark blue he will call violet. It is not surprising that the color-blind thinks other people are seeing colors exactly the same as he does. Dr. Pole remained unaware of his defect for thirty years, and Dalton did not discover his peculiarity until he was 26. Further, it is possible, for a color-blind who is aware of his abnormality to hide his defect in everyday life and he can very often do so with surprising skill.

Sometimes, instead of the green being substituted by yellow it may appear as grey. Thus, if a grey piece of paper is presented to a color-blind he may describe it as a green.

The general finding, which we hope is gradually gaining ground, is that there are different degrees of color-blindness extending from extreme cases, in which blue and yellow are the only two colors visible, to milder cases in which the blindness to red and green is not total. In these milder cases the person can see red and green if they are bright enough or vivid enough. It is these milder forms which constitute the great practical problem, for the person's ability to distinguish between red and green is likely to fail when they are fatigued, or when the illumination is poor as in a mist or fog. The extreme cases can be easily detected. The milder cases, who are nevertheless dangerous color-blinds require more careful examination if they are to be detected.

Testing Color-Blinds

These milder cases show all the characteristics of color-blinds and make the same typical mistakes. They must not be confused with cases of anomalous vision. Rayleigh, in 1881, found that a number of persons with otherwise normal color-vision were equally sensitive to red and green. In equating red and green equal to yellow (since known as the Rayleigh equation) some were found to require far more red than the normal, others required an excess of green.

The testing of color-blinds presents a problem of great practical importance and a certain technique has to be adopted. Color-blinds avail themselves of all kinds of secondary aids to enable them to discriminate color. If a color-blind were shown two pieces of paper and was told that one was a green piece and the other red, and if these papers were then mixed up with some other colors, he would probably be able to identify them correctly because he had made use of some identifying mark in the paper, perhaps undetected by the normal observer.

An employee in a printing house was found to be color-blind, to the great astonishment of his fellow workers. His duty was to cut up colored carboard and paper. He always managed to use the correct colors because they were always kept in certain positions on the shelves. It was a simple matter to reveal his defect by altering the position of the colors.

Stilling's Test

A certain skill is necessary in devising a test. It must be such that it will offer no guidance to the color-blind in the discrimination of color, but he will have to fall back entirely on his color sensations. Many are apt to think that a color-blind guesses the names of colors; he may in an emergency, but generally he has a definite regular color system to which he rigidly adheres.

1. *Stilling's Test.*—This is a test which is very useful for detecting color-blindness. It does not give much information about the nature of the defect, but merely shows its presence. There are 14 tables in all, based on a certain principle. We have seen that all the colors on the one-half of the spectrum appear alike, except that they differ in brightness or in shade. Now, if we make the two colors the same shade we shall puzzle the color-blinds. If we had a dark red and a medium shade of green, then a difference would appear in shade which could be detected by the color-blind, but if we make the shade of both colors identical we are taking away the secondary means of distinguishing the colors. This is the principle in this test. Green figures are superimposed on a red background, for example, the red and green being of equal brightness. A number of tests are based on this principle.

2. *Wool Test.*—Another type of test is based on comparison. The color-blind person is not allowed to remain passive, but is asked to do something and by his own actions his defect is revealed. The simplest test, modified or in its original form, is the wool test. One hundred and fifty skeins of wool are spread out before the examinee in a good light. These are known as "confusion" skeins. A test skein is given to him, no name is mentioned, and he is asked to pick out all the colors which resemble the test skein, irrespective of shade. The numbers of the skeins he selects are noted and also the numbers of those he rejects. The color-blind are very careful in matching colors and evince great dissatisfaction if their matches do not please them.

The names given by color-blinds to some of these skeins are interesting. Very pale greys, drabs and creams are usually thought to be pale pinks or pale greens. A characteristic nomenclature is as follows: pinks are called blues, reds are called browns and greens are called yellows. Orange cannot be distinguished from yellow, nor purple or violet from blue. Reds and greens change names promiscuously. One subject was very proud of one color, a very dark green, which he claimed twice over with evident satisfaction to be crimson lake.

4. *Lantern Test.*—Before tests were introduced to diagnose color defects, a great number of accidents on rail and at sea were found to be caused by some color anomaly on part of the engine driver or pilot. Of late, however, tests have been made compulsory in both these vocations. The lantern devised by Edridge-Green shows the red and green lights as they appear in actual practice.

(Continued on page 542)

AMERICAN DYESTUFF REPORTER

Devoted to the use and application of dyestuffs and the mechanical equipment incidental thereto

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Published biweekly by
HOWES PUBLISHING CO., INC.
440 Fourth Avenue, New York City

A. P. HOWES, President — M. D. REESER, Secretary — H. F. CRAWFORD, Treasurer

Subscription price $5.00 per year; Canadian $6.80; foreign $6.00

Volume XXI August 29, 1932 No. 18

RAYON YARN PRICE SITUATION

RAYON yarns have shared in the general improvement in textile commodities to the extent that sales volume has jumped appreciably during the last month. On the finer deniers, notably 100s, business has been so large that there has developed an actual scarcity of quick delivery yarn. This situation, in view of what has happened in silk, cotton and wool, has naturally led to considerable speculation as to the possibility of higher prices on rayon yarns.

Much has been said and written along this line, but it appears to be the intention of important rayon producers not to make haste too quickly in working their prices to higher levels. Leaders in the field have been taking business freely at present prices for delivery through the end of the year. Those supposed to be close to the inside in rayon circles say that producers have no intention of advancing quotations in the immediate future, believing it to be good policy to get their plants back on capacity production, and to await the expected further increase in raw silk prices before taking definite action.

These so-called insiders, however, have sometimes been wrong in the past, and they may be wrong again now. On the surface it does not appear likely that rayon producers will put their prices up generally, until they are reasonably sure that the higher levels will take and hold. It is believed to be good policy nonetheless for rayon yarn consumers to keep in mind that a price of 55 cents on the basic number of rayon knitting yarn is probably just as artificially low as were $1.10 for raw silk and 5 cents and less for cotton.

SEEKING A REMEDY

FURTHER evidence that silk manufacturers and others identified with the silk industry in the Paterson district realize that drastic measures are necessary to place this industry upon a sound footing was given recently at a largely attended meeting when steps were taken to organize an association to work co-operatively toward the elimination of the present abuses in the industry, "The Morning Call," Paterson, N. J., points out editorially.

"Among the things proposed as necessary are agreements providing for a single working shift, thus eliminating the two and three shift plan operating at various times in many mills; a uniform cost system and uniform selling terms; limitation of the finished product to be kept on hand to twice the sales demand of the individual manufacturer, and the placing of a limit on the manufacture of small lots.

"In this way, speakers pointed out, price wars which have been the bane of the industry would be brought to an end, while manufacturers would not constantly be confronted by an unknown quantity of finished goods which threatened prices and disorganized systematic production.

"The several hundred manufacturers who were present seemed to realize the necessity of such a step as is proposed if the industry is to be put on its feet, and a permanent organization will be effected when it is expected that various committees named to study the problems of the industry will probably come forward with other suggestions as to reforms to be instituted.

"There is no doubt that such an organization as is planned would be a factor in the industry, not only locally but nationally, for Paterson is still the center of the industry in this country, and reforms instituted here are likely to spread to other sections.

"To this section the placing of the silk industry on a sound foundation is particularly important, for it is our principal industry and upon its prosperity depends the prosperity of every merchant in the community. With silk manufacturing again on a prosperous basis, something that has not been the case for a long time, and with silk workers faced with more constant employment and at a better wage scale than now prevails, the purchasing power of the whole community will be greatly increased.

"It has been difficult in the past to secure proper cooperation between manufacturers in this district for united action, but under present-day conditions it is evident that all those in the industry realize that a change from the haphazard methods prevailing in the past, with cut-throat competition, long hours and low wages, will have to be brought about. This is a good sign and the silk manufacturers and allied industries should have the whole-hearted support of the banks and the public at large in bringing about the proposed imrovement."

New Additions

Important additions have been made to the equipment of Alabama Polytechnic Institute school of textile engineering and will be ready for use at the opening of fall session on Sept. 6.

The additions include laboratory sized units for cloth dyeing, bleaching, and processing. Consisting of a jigger, squeeze rolls, padder, and scouring out boxes, all units are so constructed that they may be used for a complete and continuous piece-goods processing and dyeing layout or as separate units. They will be either hand-operated or motor-driven.

Each unit is so designed as to give similar ratios of dye-liquor to amount of fabrics being processed in the same manner as with full-sized dyeing machines. Shade-matching and working out of pot-dyeing formulæ on these small units will be so stressed that a student may apply the dyeing or processing formulæ on full-sized machines. This instruction will be stressed in both junior and senior textile chemistry and dyeing courses. The types of dyes covered will be representative domestic and foreign made directs, vats, sulphurs, naphthols, indigosols, and basics.

The laboratory printing machine has been refitted so that with the addition of cloth dyeing units, the Auburn school of textile engineering will have a complete layout of laboratory-sized dyeing equipment whereby printing, dyeing of cloth, dyeing of yarns in the skein form and package yarns (four types of package machines) and raw stock (cotton—three units) may be done. Two small hydro-extractors and necessary drying units complete that needed requirement.

The Ozone Process May Mean Lower Costs in Bleaching

By P. L. Mann

WHILE the major portion of cotton is bleached in the piece, the process, according to its peculiar requirements, is sometimes advantageous before the cotton is manufactured or in intermediate stages.

The over-energetic action of the ordinary chloride of lime bath on special work necessitates the use of either hydrogen peroxide or hypochloride of soda, both of which are used successfully with certain modifications.

Fundamentally, of course, all textile bleaching processes rest upon the oxidizing action of oxygen, the use of chlorine compounds being simply an indirect method of cheaply and conveniently introducing a suitable concentration of oxygen at the point where its action is desired.

The fewer unnecessary chemicals introduced into the solution which is to do the bleaching, the easier it is to obtain and to maintain the ideal chemical conditions required.

The many claims made for bleaching cotton with chlorine compounds have reason to be questioned. The old cotton and linen bleaching methods whereby the cloth was exposed to the direct action of sunlight produced excellent results, but were too slow and subject to variance in weather conditions.

Modern technology has produced the stage of development where the oxygen necessary is first produced by the reaction between chlorine and water. The method of working is subject to wide modification, according to the nature of the bleaching agent employed, and especially the state of the material under treatment.

The argument, however, that peroxide bleaching of cotton produces a permanence of whiteness over other methods is not strictly correct. Hypochlorites, permanganates, or any other oxidizing bleaching agent if properly applied will result in the same degree of whiteness.

It is interesting to know that the well known Italian cotton-spinning firm, the Stabilimenti Crespi, of Crespi, near Milan, has been operating the ozone bleaching process on the commercial scale for four years. At first only a portion of the output was treated by this method, but owing to the superiority in the white produced, the demand from customers became so pressing that the firm has now decided to bleach the whole of its output by ozone.

Lower Costs

Little is known as yet of the technical details of the method. The ozonizers employed are of the Otto type (though they have been improved by the Crespi technologists) with double dielectric, the elements of which are built up being interchangeable. The power consumption varies from 15 to 25 watts per gram of ozone produced. To obtain this efficiency the air used for ozonization at Crespi is first cooled and then dried. In the operation of the process the cotton is first boiled off in the usual way and then treated with the ozonized air. The latter, the ozone concentration of which is under positive control, is introduced into a gas-tight vessel in which it pursues a course in counter-current to the cotton yarn. The duration of contact for satisfactory bleaching varies with the type of cotton, but for Indian cotton it is said to be from forty to sixty minutes. The finishing operation is simplicity itself and consists of water rinsing.

The practical results of the process are said to be extremely satisfactory. Not only is the white produced whiter than obtainable by other methods, but there is absolutely no impairment of the mechanical and physical properties of the fiber, the possibility of the formation of oxycellulose is altogether ruled out, and, finally, the loss of weight sustained by the fiber in the process is less than with any other known bleaching process. The textile industry in this country will await with interest further news of this important development, particularly as it claimed that bleaching costs are reduced by the ozone method.

Detection and Estimation of Chemical Damage in Wool*

By **PROF. DR. P. KRAIS**

Deutsches Forschungs institut fur Textilindustrie, Dresden

To be able to estimate the amount of damage which is done or may be done to the wool fiber during the various alkaline, acid, reducing and oxidizing processes it has to undergo during the manufacture of fabrics is a matter of importance and has been for a long time. Numerous proposals have been made in this direction. Color reactions, the action of chlorine water, the coupling with diazo compounds, the estimation of soluble nitrogen, the biuret, sulphide of soda, bichromate and other reactions come to mind.

WE DO not think much of color reactions in these cases, because they seem sometimes to give an exaggerated idea of the damage, and we do not think the industry should be alarmed without urgent need and without giving unmistakable proof.

Therefore, we maintain that any color or chemical reaction which is to be accepted, must be corroborated in full detail by mechanical tests. It is not the chemical behavior but the mechanical strength and elasticity which count in practical use.

Still there is another point. We have observed that there are chemical damages, especially by alkali, which do show in the amount of soluble nitrogen, but have no effect upon the mechanical properties, unless an acid treatment, such as dyeing at the boil with sulphuric acid or bisulphate, has followed. These latent faults are, of course, very tricky. They do not show if you test the fiber mechanically in the dry state, but they show strongly in the wet state, the strength of the yarns as well as of the single fibers being considerably affected.

By the determination of soluble nitrogen we understand the method first proposed by O. Sauer in 1916, and simplified by Krais and Schleber in 1929. The total nitrogen contents are first determined by the Kjeldahl method, and then small quantities of the original and of the treated samples are kept in a solution of alkali and hydrogen peroxide for three days, then filtered, washed and the filtrate acidulated and kjeldahled. (Exactly: 0.1 g. of sample with 8 c.c. water, 10 cc. 1 per cent hydrogen peroxide and 2 c.c. n/2 potassium hydrate solution.) The nitrogen going into solution (in form of ammonia, aminocarbonic acids, etc.) is calculated in per cent of the total nitrogen. Thus we find in a fine wool about 4 to 5 per cent soluble nitrogen in the original, in the damaged wool a rise up to 32 per cent and more.

Chemical and Mechanical Tests

We give now two examples, which show the relations between chemical and mechanical tests. A fine wool of 24.9*u* hair diameter (average of 1,000 measured fibers) and a 10 m. weight of 6.515 mg., corresponding to the metric Number 1535, and a coarser wool of 32.8*u* diameter, a 10 m. weight of 9.85 mg. and the metric Number 1015 were treated as follows:—

I. Alkali: 3 hours at 80 deg. C. in 3 per cent sodium carbonate solution.

II. Bleach: treated cold with a 0.1 per cent potassium permanganate solution with excess of sulphuric acid, then with bisulphite and sulphuric acid.

III. Weak acid: boiled for 2 hours in a 0.2 per cent sulphuric acid solution (reflux cooler).

IV. Strong acid: boiled for 10 hours in a 0.5 per cent sulphuric acid solution.

After treatment the samples are rinsed and dried at ordinary temperature.

Of the figures under 2, 3, 5 and 6 in the table is to be said that they are averages of 25 to 30 dates each. Of every sample about 130 fibers have been gummed on to paper frames of 1 cm. free width, then the diameter has been measured and only those fibers have been tested, the diameter of which was within ± .2*u* within the average diameter.

For the wet tests under 3 and 6 the fibers were wholly immersed into a 1 per cent solution of Nekal BX for one minute and then tested in the immersed condition.

The classification of the extension curves, as given under 8 to 13, was made so that the fibers showing all three periods (slow, quick, slow), which are found in the sound wool hair, were called "good," those showing

*Paper read at Textile Institute Conference at Leamington Spa on May 20.

DETECTION AND ESTIMATION OF CHEMICAL DAMAGE IN WOOL

		—Fine Wool Treatments—					—Coarser Wool Treatments—			
	Original	I	II	III	IV	Original	I	II	III	IV
1. Soluble Nitrogen per cent.....	3.42	3.91	3.77	3.91	9.58	3.38	3.82	3.70	4.95	9.64
2. Breaking strength in g. dry...	11.2	11.7	10.3	11.1	6.7	19.9	16.3	21.6	19.1	10.4
3. Breaking strength in g. wet...	8.3	5.6	6.7	7.5	3.7	15.3	10.2	14.6	12.4	4.6
4. Per cent wet of dry strength..	74	48	65	67	55	77	62	63	65	44
5. Extension at breaking point in per cent dry	38.5	33.8	35.3	33.3	3.2	43.7	38.5	33.1	41.0	24.2
6. Extension at breaking point in per cent wet.....	63.6	51.2	55.8	50.5	34.1	66.6	61.1	64.5	53.2	39.0
7. Increase wet in per cent.....	65	51	58	51	970	52	59	95	30	60
8. Extension curves *dry*: good..	82	52	70	55	—	94	81	94	94	33
9. Extension curves *dry*: middling	18	22	20	33	3	6	15	3	3	33
10. Extension curves *dry*: bad....	—	26	10	12	97	—	4	3	3	33
11. Extension curves *wet*: good...	96	97	100	100	42	100	100	100	94	88
12. Extension curves *wet*: middling	—	3	—	—	42	—	—	—	—	12
13. Extension curves *wet*: bad....	4	—	—	—	16	—	—	—	6	—
14. Breaking length in km., dry..	17.4	17.9	15.8	17.0	10.3	20.2	16.5	21.9	19.4	10.6
15. Breaking length in km., wet...	12.7	8.5	10.3	11.5	5.6	15.5	10.3	14.8	12.6	4.7

only two were called "middling," and those breaking within or shortly after the first period were called "bad."

The breaking length (14 and 15) in km. is found by multiplication of the metric number by the breaking weight.

The apparatus we used is described in the *Journal of the Textile Institute*, 1928, p. T32.

It seems that, looking over the figures of the table, one might give up even the nitrogen method as too little differentiating, and rely exclusively on mechanical testing. And here we think that the classification of the extension curves and the comparison of the breaking strength in g. or the breaking length in km. of the single fibers in the dry and wet condition gives us a very good measure indeed of the amount of damage done to the fibers.

In general we may say the coarser wool is less affected by chemical treatments than finer wool.

Anomalies and Defects of Color Vision

(Continued from page 538)

Testing for color-blindness should be carried out periodically, for although in general the defect is innate, it may in certain cases be acquired. The disease in such cases is progressive and so may remain undetected for some time. This form of color-blindness may be caused by over-indulgence in tobacco, or by excessive use of a drug, such as santonin. Such cases are curable.

GROUP TEST

4. *Collins-Drever Group Test.*—This is for use in schools. Numerous examples could be given of a boy being trained for an occupation which later he has to discard because of the discovery that he is color-blind. The way to avoid such waste is to test every boy and girl while at school for the presence of color-blindness and to advise against any occupation in which color discrimination is an absolute essential. This test can be given to small groups of ten or so at a time. It is based on the same principle as the Stilling tests and consists of a color letter on a colored background. The letter can be rotated and appear in different positions, which the child is asked to draw. The test is also suitable for adults.

Swiss Output Drops

Swiss silk and rayon weaving establishments are reported working at only about 50 per cent of capacity. In 1929, the latest census year, there were 79 such firms, employing 12,557 workers, according to a report by the Bureau of Foreign and Domestic Commerce of the United States Department of Commerce. At present, thousands of looms are standing idle, and the number of workers has been reduced at least 2,500. Some plants have suspended operations.

Notwithstanding heavy declines in exports of silk goods and increased imports, the Zurich Silk Industry Union, nevertheless, believes that as soon as normal conditions return, the idle looms will be set in motion and also that the accumulated stocks, made of raw material bought when prices were exceptionally low, may bring a good profit later.

The report of the Union adds, however, that Switzerland will be able to compete successfully in foreign markets only if cheaper production costs can be attained.

Technical Notes from Foreign Sources

Notes on the Preparation of Artificial Silk with Linseed Oil

K. Swoboda—Kunst-Seide 13,101 (1931)—The need for a finishing agent for artificial silks was not foreseen and at once met, at the beginning of the new industry, but was recognized only after trouble had been encountered in spinning and weaving. The use of a linseed oil preparation consists in something more than simply "greasing" the yarn so that it will pass easily through the machinery; it consists in a kind of gumming together of the separate fibers in the yarn intimately, and at the same time surrounding the yarn with a thin, elastic membrane, which protects the fiber-bundle in a way hardly attainable by using preparations of glue, gelatine, starch, etc. The linseed oil finish is absolutely the best as far as the mechanico-textile side is concerned, but not so good when such material is to be dyed, as it is well known that linseed oil, on exposure for a reasonable time to air, becomes oxidized, thickens, and finally hardens to a rather resistant coating difficult or very difficult to remove; in extreme cases it cannot be removed entirely, at all; this is especially true when yarn so prepared is stored for a considerable time. In other words, the ordinary linseed oil preparations would be altogether ideal, for all branches of the industry, could the manufacturers be sure that the yarn would be sold, knitted or woven, and dyed, within so many days of its preparation; but such a possibility never has and probably never will be existent.—The presence of any oily dressing upon goods to be dyed in an aqueous bath, as is always the case, is too well known as one of the most fruitful causes of uneven dyeing.

Linseed oil, according to reliable sources, consists approximately of 8% of the glyceride of palmitic acid, of 15% of that of oleic acid, 25-30% consists of the glyceride of linolic acid, and 35-40% is the glyceride of linolenics acid. There are other components present in much smaller quantity, such as the glycerides of stearic and arachidic acids. Of the principal constituents, oleic acid contains one double bond, linolic acid two, and linolenic acid three. Such glycerides are what form drying oils, oxygen being taken up by them at the double bonds, the oils passing over into more or less saturated compounds, of a resinous nature. For use as drying oils proper (e.g., in paints), minute amounts of catalysts, lead or manganese oxides, are added, to hasten the process of oxidation, or drying. When this is accomplished, these catalysts do not cease their action, but slowly transform the oxidized glycerides further, to peroxides, organic aldehydes, acids, etc. Such catalysts are frequently found in the linseed oil used for the preparation of artificial silk. From the above well-known facts, it is evident that (1) linseed oil oxidized to the acid stage (this does not mean by any means completely oxidized to nothing but organic acids, but, at the least, oxidized to such a point that these acids have begun to form) will have a damaging effect upon cellulose fibers, since nearly all organic acids do affect the tensile strength and elasticity of artificial silk unfavorably; (2) the oxidative process may well proceed from the oil layer into the surface of the fiber, and begin to break this down by oxidation (cf. the formation of organic peroxides as part of the process of "drying" of the oil), and so weaken it and alter its affinity as well toward dyestuffs.

These two general facts, considered in connection with the usual difficulty of removing the coating of a linseed oil mixture from the fiber, show how serious the objection is to the use of drying-oils for lubricating or finishing purposes.

If, however, in order to avoid as far as possible the formation of a tough membrane of dried oil upon the fiber, the linseed oil is diluted to a proper degree with some half-drying oil, such as Soja oil, or with some non-drying oil, the resinification of the linseed oil upon the fiber cannot proceed so rapidly or so far, so that removal of the oily coat is easier and safer, and can be carried out with a lukewarm soap bath, or with weak ammonia water. Further, by such a dilution of the linseed oil, since its rate of oxidation is slowed down and inhibited beyond a certain point, the formation of dangerous organic acids is correspondingly diminished, and what does form is in a more diluted form, owing to the presence of the half- or non-drying oil; and, again, the extension of the oxidation to the fiber is prevented or hindered.

In any case, care should be taken that yarns finished with any kind of linseed oil preparation be not scored for unreasonable lengths of time.

In reference to the method of applying the oil-preparation, the older one, of impregnating the fiber with a solution of the oil or oils in some solvent, such as benzine, benzene, tetrachloride, etc., and then centrifuging and drying, is the better. The newer method, that of applying the oil in an aqueous emulsion, has the disadvantage that the oil does not penetrate the fiber so deeply, and tends to remain as a more or less superficial coating.

Uneven Crepe-Effect in Mixed Weaves

Deutscher Faerber-Ztg. 67,168 (1931)—A case under investigation consisted of a mixed weave, whose warp was of acetate silk, and whose woof was of viscose crepe-yarn. Here and there in the goods there occurred narrower bands, which were most noticeable by the differ-

ence in their luster, as compared with that of the main part of the fabric. It was found, upon study, that the twisted yarn of the viscose crepe wool had, in several places, not been dyed by the dyestuff which had been used to indicate the direction of the twist of the yarn. The undyed portions had simply not taken up the dyestuff, because they had not been wetted out so readily as the part which was normally dyed. Now, it is well known that artificial silk, in the wet condition, has elastic properties other than what is the case in dry fiber. The internal tension of the parts of the yarn which remained undyed was therefore different from that of the dyed yarn, and so, upon crepeing, such parts behaved differently from the normal portions. The undyed portions, even before crepeing, showed a tendency to curl or crisp, and so, in the fabric, such parts displayed a difference in luster. The whole trouble was traceable back to unskilful wetting-out before dyeing to indicate the direction of twist of the yarn.

Degumming of Natural Silk in Presence of Acetate Silk

Dr. H. Schmidt—Monats. f. Textil-Ind. 47, 14 (1932). —Experience has shown that it is best to work up raw silk in that condition, and to degum it only after the completion of the weaving. As the use of acetate silk in combination with the natural fiber is increasing, the danger of saponifying the acetate silk during the degumming has presented a new problem. There are two procedures now being used to avoid this danger; one originating with Dreyfus, and the other with the chemists of the I. G.

Dreyfus employs a bath containing sulphonated fatty acids or their salts, to which sodium silicate, carbonate, or borate is added. Treatment is at 75° C., with a 40-50% solution of Turkey-red oil, containing the above sodium salts at a concentration of 10 g. per liter. After impregnation with this bath, the goods are squeezed to a gain of 40-50% on the weight of the goods, then rolled for several hours. Finally, the goods are rinsed in a 5% soap solution, at 75° C., twice, the soap baths containing additions of the same sodium salts as above, at a concentration of 0.3 g. per liter. D. found later that the soap solution ordinarily used, which is an excellent means for removal of sericine from raw silk, will not have any effect upon acetate silk if the hydrogen ion concentration does not exceed 10.5. Degumming of the natural silk in union with acetate silk can take place, with safety to the latter, if soap baths of a hydrogen ion concentration of 10.0-10.5 are used, at 75° C.

A typical example of D.'s method is as follows: for a mixed weave of one part of natural to two parts of acetate silk (which is just as effective for pure natural silk or mixed weaves of it with cotton, linen, wool, or viscose) a bath of 5.0 g. of soap per liter at a bath ratio of 60-1, is used; if the hydrogen ion concentration is not correct, it may be adjusted by addition of sodium phenolate. The goods are treated for 3-4 hours at 80° C., the alkalinity of the bath being maintained within the necessary limits by occasional addition of sodium phenolate. Finally, the goods are rinsed at 80° C. in a bath of 2.0 g. of neutral soap per liter, in order to remove mechanically adhering solid matter, then washed and dried. The bath can be used repeatedly by after-freshening. If a matting effect is to be imparted to the acetate silk, the temperature must exceed 80° C., and the concentration of the soap bath must be increased until the desired effect is attained; for example, with a mixed weave of equal parts of natural and acetate silks, the soap bath is of a concentration of 5.0 g. per liter, as before, the alkalinity is kept at about 10.0 by addition of dilute caustic soda solution, and the 3-4 hour treatment is carried out at 95° C., caustic being occasionally added to maintain the desired alkalinity.

The I. G. method consists in the treatment of the mixed weave with solutions of acids, in the presence of sulphonated oils, fats, or fatty acids, which are stable toward free acids, in this case:

(a) for a mineral acid, the goods are treated for 2-3 hours in a 1-40 bath, which contains 5-15 c.c. of concentrated HCl and 15-25 c.c. of sulphonated oil, each per liter, the proportion of each of these components varying according to the condition of the natural silk. The goods are then rinsed, and soaped for 1-2 hours at 60°-70° C., in a 1-40 bath, in a fresh solution of Marseilles soap of 10 g. per liter; then rinsed again, and dried.

(b) for an organic acid the bath might contain 4-5 c.c. of glacial acetic acid and 2-3 c.c. of sulphonated oil, each per liter, in a 1-250 bath, at 80° C., for 2-3 hours. Then, after rinsing, follows treatment for 1-2 hours, at 60°-70° C., in a bath containing 1-3 c.c. of sulphonated oil and 5-10 g. of Marseilles soap, each per liter; and rinsing and drying as before.

Degumming and bleaching of natural silk in a mixed weave, according to the I. G. method, can be carried out simultaneously by the use of a protease extract. For example, the goods may be treated in a bath containing 3,000 parts of 0.1% salt solution, 5.0 parts of commercial papain, and 0.2 parts of hydrocyanic acid, for one hour, at 60°-70° C., then worked for a short time in a cold soap bath, and then rinsed with water. This method works well even in the case of weaves where the silk yarn has been given a strong twist, or where the sericine is in other ways mechanically somewhat protected; also, when the silk has been prehardened by use of formaldehyde. It is also satisfactory in cases where the raw silk has been dyed. Pancrease may be used instead of protease, with as good results.

Vat Dyestuffs (Benzanthrone Series)

German Patent No. 454,427 (22/XII/'27)—*I. G. Farben-Ind. A.-G.*—When phenyl-benzanthrones are heated with anhydrous aluminium chloride, certain characteristic condensation-products are obtained, which, when fused with alkaline condensing agents, as caustic alkalies, so-

dium amide, potassium anilide, etc., yield vat dyestuffs. These are present in the melt in the leucoform, in combination with the caustic alkali, and when the melt is dissolved in water and aerated, oxidation to the dye-form occurs, and the dyestuff precipitates out. The products are in the blue range of the spectrum.

Removal of Oil and Grease Spots

Monats. f. Textil-Ind. 47, 24 (1932).—In response to an inquiry in the correspondence columns of the Monatschrift, upon the topic cited, there are two replies given, which show a not infrequent difference in point of view. The topic being one of great interest and importance, the two are worth quoting:—

(a)—"A.M." uses, for the removal of spots, Perpuril T.F.O. (marketed by an Augsburg firm), and is "very well satisfied with it. Spots can be removed from goods very easily, without delaying the course of operations." he claims.

(b)—"ph"—"From the quesiton, it is not plain what the origin of the so-called spots is; but such knowledge is necessary for an exhaustive reply to the question. It is not a matter of indifference whether the spot is of an animal, vegetable, or mineral, or of some 'chemical' nature, or whether the oil or grease spot is accompanied by dirt, iron-rust, etc. Certainly, there are many solvents for the purpose of removing oil and grease spots: benzine, Benzinoform, benzene, chloroform, Dedaclorin, Edesform, Hydraphthal, Laventin, Legia Soap methyl-hexalin, pinol, Perticol Soap, Tetrapol, Tetralix, Tetralin, Turkonoel, Verapol, and a number of others; but a complete removal of all sorts of spots which may occur has not yet been found possible, as far as I know, with any of these agents. When such spots are present, it is important to know whether they are still fresh, or whether the goods have been stored for some time, with the spots on. In the latter case, the removal of the spots is more difficult, since the substance forming the spots will have worked its way into the material. With most of the agents mentioned above, a previous rubbing of them into the spots is requisite, if the removal of the spots is to reach a definite degree of completeness.

"A really good agent for the purpose is prepared as follows: 15 g. of Marseilles or Venetian soap are dissolved in 250 c.c. of warm water, and to the cooled solution are added 50 g. of ethyl acetate, 50 g. of ammonia water, and 10 g. of oil of turpentine; this mixture, in a flask holding a little more than a liter, is then made up with water to 1,000 c.c., and the flask tightly corked. Before use, the mixture is to be well shaken. Fresh oil or grease spots are easily and completely removed by this mixture. If the spots are of animal or vegetable nature, it may be necessary to treat them first with dilute caustic soda solution and then wash with one of the soaps specially prepared for the purpose. If the spots are of mineral origin, it may prove impossible to remove them by even the most vigorous means, even by treatment with an alkali, or by boiling under pressure. From what has been said, it will be seen that the removal of spots, taken as a general proposition, is not to be carried out merely by rubbing with some spot-remover. Spots on fabrics are more easily avoided than removed."

Effect of Common Detergents upon Acetate Silk

Dr. A. Lauffs—Deutscher Faerber-Ztg. 68, 181 (1932).—F. Ohl has recently made some observations upon this subject, and has come to the conclusion that there is available as yet, no absolutely ideal cleansing agent for acetate silk. Dr. Lauffs does not agree with the point of view adopted; and goes on to discuss Ohl's work.

(A footnote states that an article upon the same topic appeared not long ago in a German textile journal, but that it did not appear pertinent enough to deserve comment in the Faerber-Zeitung. The editor remarks wisely, "In reference to the action of cleansing agents which bleach as well as cleanse, it seemed to us that a one-sided treatment of the subject, very surprising to an expert, was in evidence. Peroxide bleaching agents are well known to the mildest of all bleaching agents, even when used in the strongest baths; and the consideration must occur that, in their use as cleansing agents, therefore in only very small quantities, this characteristic would at once change, to some degree. An experienced man has at his disposal, frequently enough, agents which do not act in a general way so favorably, but which can be used without any damage resulting. In washing, bleaching, dyeing, and in fact any kind of treatment, it is a primary consideration that just the correct quantity and ratio be employed. In any other case, even the best dyeing, bleaching, and cleansing processes will not lead to the desired results.")

Ohl's work differs in important details from the usual form of procedure as it is followed in practical work. To be sure he has worked with agents commonly employed in technical work but has not regarded the rules for use which have been worked out in the industry by practical experience. It is not surprising, therefore, that he has obtained unsatisfactory results, since the usual standards of concentration, temperature, and time-factor have been extensively disregarded. Thus, in practice, solutions of 0.5-1.0% are used. O. has worked exclusively with 2.0% solutions; thus involving two points; that a 2% solution of a cleansing agent has hardly any more cleansing power than has a 1% solution and that, from the cost standpoint, perhaps as much as 50% of the amount of agent used would therefore be simply wasted. O. grants, in fact, that the cleansing of acetate silk is easier than that of any other fiber, since, owing to the comparative non-porosity of the fiber, the particles of dirt, etc., are practically only adherent to the surface of the fiber, and not entangled within its interstices, and so are more easily dislodged; which would make unnecessary any such over-vigorous treatment as he employed. Neither a higher concentration or a higher temperature, or a longer treatment, should be necessary. Also, the

temperature of 45° C., chosen by Ohl, is unnecessarily high, since acetate silk goods, in practice, are satisfactorily cleansed in cold, or at most in merely lukewarm, baths. Still again, Ohl's time factor of 60 minutes is excessive, at least at a temperature of 45° C.

The unsatisfactory results obtained by Ohl may also be explained by the mechanical treatment to which the materials used were subjected let it be remembered, for one hour, at 45° C., in a double-strength solution. It should hardly require mentioning, nowadays, that acetate silk, as all the artificial fibers, is very sensitive to mechanical influences while in the wet condition. No practical worker would handle or work artificial silk thus, for a whole hour. Really, considering the factors used by Ohl, of time, temperature, concentration, and mechanical working, it does not seem that any conclusion either as to the effectiveness of the cleansing agents used, or as to the resistant power, or quality, of acetate silk can justifiably be drawn. In addition, O.'s unfavorable conclusions were based upon work with acetate silk which he himself had prepared; when he afterwards worked with commercial material, his results were better, though as to this he gives no figures.

In regard to the question raised by Ohl, it is rather evident that it is possible to cleanse the commercial acetate silks now on the market, with good commercial detergents, in a satisfactory way. Two well-known textile experts, whose reputation for conservativeness and accuracy would make even a bare statement from them, unsupported by experimental figures, worthy of belief, have published certain investigations recently, namely:

(a) Krais and Markert, in the Monatschrift F. Textil-Industrie (Vol. 1930, p. 329), working with Persil, upon both natural and artificial silks; cupro, viscose, and acetate silks. In brief, they subjected the materials to a 30-fold repetition of treatment, and found no loss in tensile strength, etc., to have resulted. No unfavorable results were found to follow from their treatment, in any direction.

(b) H. Brandenburger, in the Zeitschrift f.d. ges. Textil-Industrie (Vol. 1932, p. 112), worked with Persil and with soap, upon acetate silk; and in his emphatic way states "It has become possible, merely from this series of experiments alone, to prove that oxidative cleansing agents, of the class of which Persil is the best-known member, produce no stronger influence upon dyeings on acetate silk than do the purest soap solutions. It can further be asserted, in view of their characteristic composition, that they specially suppress the tendency of the dyestuffs to dissolve off." From this, it is clear that B. found no tendency toward saponification of the surface of the acetate silk fibers.

The concurrence of two such well-known workers, each equally known as theorists and as practical men would seem to show that ordinary, rational working with modern cleansing agents is perfectly safe and satisfactory, even with acetate silk.

Developing Dyestuffs (Nitrosamines)

German Patent No. 448,426 (18/VIII/'24)—*Dr. Hans Bucherer, Munich.* — An extension of the nitrosamine method. The nitrosamines are prepared as usual from suitable desired primary amines, and are used in weak served for use), preferably through the presence of sodium carbonate. These nitrosamines are characteristically alkaline reaction (in the condition in which they are preslow in coupling, or do not couple at all, while alkaline, at the ordinary temperature. Their principal advantage is their keeping quality. The point of the present patent lies in causing them to react at a high temperature at about 100° C. with desired second components, in which case they react directly, without the need of rearrangement to the ordinary, actively coupling, diazo form, which usually has been brought about by previous treatment of the nitrosamine with an acid, an acid salt, or at least a compound capable of neutralizing the alkali of the nitrosamine.

As coupled in the alkaline, nitrosamine condition, the coupling does proceed more slowly than in the acid, active condition, but smoothly and satisfactorily. Points to be observed are, the avoidance of much free caustic alkali, and the use of the high temperature mentioned, 90°-100° C.

Developing Dyestuffs (Naphthol AS Series)

German Patent No. 448,761 (18/VIII/'27)—*I. G. Farben-Ind. A.-G.*—The patent relates to the Naphthol AS products, in particular the 2-3-hydroxynaphthoic arylides of primary diamines. When such products are used as second components with diazotized primary amines, whose solutions have been made neutral or alkaline, the pigments generated in the fiber display an as yet unattained fastness to kiering, and also very good fastness to chlorine. Aniline and its homologues are specially mentioned as suitable for the diazo-component; varying tones may be obtained by mixtures of different amines.

New Methods of Treatment of Animal Fibers

G. Choisy—Tiba 9, 721 (1931)—A discussion of French Patent No. 704,423, of the I.G., which we have as yet not seen.

The patent covers certain new methods of treating animal fibers, particularly wool, in order to impart to the materials properties, in luster, flexibility, and feel, differing from those of the untreated fiber. Sodium sulphate, urea, Iceland moss, starch, etc., have been employed for similar purposes before now, but their action has been of a more or less physical sort; and the great disadvantage involved has been, that goods so treated, if exposed to the action of water, lose the characteristic properties which they have gained; the goods become soft, wrinkled, and hang badly if they have been worked up into garments, etc.

The new procedure consists in the treatment of the material, in a hot bath containing an organic substance of a high molecular weight, of a general acid nature; for

example, such substances being suitable as possess a natural affinity for the material; the substances employed do not color the material, or at least do so to only a very slight extent. In general, the higher the molecular weight of the charging material employed, the more solid is the effect. The substance employed may be applied either in a bath as ordinarily, by foularding, or by printing, and may be fixed further, if possible or advisable, by steaming. Suitable substances may also be applied conjointly with the dyeing process, the dyebath in that case containing also the charging agent. The goods gain in weight by the treatment, to an extent depending upon the nature of the impregnating agent, the amount of it used in the treatment, etc. Water and soaping have very little effect, in some cases no effect, upon the results.

Some examples given in the article are as follows:—

(1)—100 kilos of wool in staple are boiled for 1 hour in a bath containing 50 kilos of 2-3-6-trichloraniline-4-sulphonic acid and 10% of sulphuric acid of 66°B., then rinsed thoroughly. The treatment increases the weight of the wool by 19%, and the material becomes fuller in consistency. It loses only a little of its weight on washing. Instead of the trichloraniline-sulphonic acid, its benzoyl and similar derivatives may be used; the results with these agents are still more satisfactory—still more resistant to water.

(2)—100 kilos of wool are boiled for ½ hour in a bath containing 50 kilos of 2-4-dichlorbenzoyl-1-8-amino-naphthol-4-6-disulphonic acid (the benzoyl group probably substituting the amino-group), and 50% of sulphuric acid of 66°B. The weight of the material is increased by 20%; the feel of the wool is better.

Other impregnating agents are trichlor-naphthalene-sulphonic acid, the condensation product obtained from 2-4-dichlorphenol and benzaldehyde-o-sulphonic acid, the condensation product obtained from sulphonated phenol and chlorbenzoyl chloride, tetrachlor-phthalic acid, and chlorinated stearic acid containing about 50% of chlorine. Other substances, similar to the last, which may be used, are chlorinated products of the fatty acids derived from fish oils, oleic acid, soja oil, ricinoleic acid, etc. Such products as these may also be sulphonated, which process of course gives them still greater affinity for wool, etc.

It would seem, though in lack of positive evidence, that such a treatment of wool, at least, with such agents, really leads to the conversion of the animal fiber into an actual chemical derivative of the wool substance, still retaining the general properties of wool, but differing in its less variable physical properties. It would be interesting to learn, by comparative dyeings with a series of representative dyestuffs, whether there would be any distinguishable difference in the affinity, and the color-tone obtained, as between treated and untreated wool.

Aloes, the Coloring Matters of

B. B.—Tiba 9, 711 (1931)—A short, descriptive treatise upon the above substance.

The substance itself, an extract of the leaves of several species of Aloe, is better known in medicine as a powerful purgative, still in good standing and rather widely used in proprietary laxatives, though not so much prescribed by physicians as was the case in the days of more vigorous medical treatment. As a drug, of formerly great importance, it was subjected to investigation as to its active constituents, a good many years ago. The principal constituent is a glucoside, aloin, the chief component of which is a derivative of anthraquinone; by oxidation with nitric acid, which also nitrates it, the substance yields a number of other derivatives of some interest; aloetic acid, a dihydroxy-tetra-nitro-anthraquinone, and chrysamic acid, $C_{14}H_2(NO_2)_4(OH)_2O_4$.

As to coloring-matters derived from aloes, one might expect what is the case; that, in earlier years, in the days of few synthetic coloring-matters, and the common use of natural ones, most of them of poor fastness and unimpressive tone, much attention should have been paid to its possible use as a dyestuff or source thereof. Boutin, in 1840, was the first who studied its possibilities seriously; Sacc, in 1854, did perhaps the most work upon it, showing that in various ways an interesting series of tones could be dyed with it; rose, hortensia, Corinth, violet, gray, puce, maroon, cannella, wood, olive, myrtle, orange, yellow, etc.—some of the names appearing so odd and unfamiliar that they might have some appeal if used to designate some of the modern popular "mode" tones. Chrysamic acid is the derivative most ready to produce this range of colors.

It is not surprising that the results were in former times rather satisfactory, considering that one was dealing with anthraquinone derivatives. The substance does not appear, from this paper, to have been used by vatting, as might have been expected.

Leather Dyeing

L. A.—Deutscher Faerber-Ztg. 67, 637 (1931) — In general, one has to distinguish between leather tanned with tan-bark or sumac, chrome-tanned leather, chamois, and glacé leather; the technique employed has also to be taken into account. The leather, of whatever sort, has in addition to be carefully graded according to thickness and color, and then to be plumped, in order to free it from dirt of various kinds, and from excess of the tanning agent, which still remains in it. A careful preparation of the material is important, if mishaps in the dyeing are to be avoided. The leather must have been exposed uniformly in the tan-pits, in order to assure uniform absorption of the tanning-agent; no acid of any kind can still be present, and all of the impurities of a chemical nature, usually present in ordinary leather, must be removed. Still further, the leather must be of a good, light color. If the leather is spotty, it must be soured with dilute sulphuric acid before the plumping; if the leather contains any fat or oil, it must be defatted with a weak soda-solution.

For the actual dyeing, either acid or basic dyestuffs are used, or both together, depending upon the effect desired.

Which to use is sometimes decided by the desire for a light or a deep tone. Calf-, goat-, and sheep-skins are usually dyed in trough, according to the so-called dip-method; the plumped skins, in pairs, with the flesh sides facing, are immersed, and dyed to the desired depth of tone at about 45°C. In this method, basic dyestuffs would be used, with no assistants; where acid dyestuffs are employed; a little sulphuric or formic acid is added to the bath. A bath of about 6-8 liters should be enough for an average pair of fells. If the flesh side is to be dyed also, we have to use either a plumping-machine with a hollow axle, or a reel. In the plumper, from 50 to 100 fells can be dyed at one time, and only about 1.5 liters of bath per fell will be need. If the leather is to be dyed only on the outer side, or if one is dealing with heavy kinds of leather, as pigskin or horsehide, the brushing-on method is generally used; and in this case the fell must either be stretched upon racks while being dyed, or else dried in the stretched condition afterward. Pit-tanned leather usually displays an uneven absorption of the tannin, and that of course means uneven absorption of the dyestuff, which shows up, obviously, in areas of differing intensity of shade. A fell thus unevenly tanned must be thoroughly soaked out in the plumper with several changes of water, and then spread out upon the work-table and properly worked up. It is best to subject the well-soaked leather to a second tanning with sumac, provided that the first tanning was not carried out with that material. The advantage of this treatment is, that the leather not only becomes lighter in tone, and softer, but its whole outer layer is filled evenly with a layer of tannin, which greatly favors even-dyeing—it is a sort of mordanting, as a matter of fact, in a special way, for a special purpose. Such a treatment with sumac extract makes unnecessary any other treatment for the purpose of lightening the color of the leather. If this sumac treatment is omitted, the tone is often lightened by bleaching, which is not a particularly satisfactory procedure, since it results usually in making even absorption of the dyestuff by the surface of the leather more difficult. Natural-colored leather, however, may be bleached satisfactorily. But the sumac treatment is nevertheless most strongly to be advised in all cases.

As to the dyestuffs used, some natural coloring-matters are occasionally employed, but mostly the modern, synthetic dyestuffs. The removal of excess tannin from the leather before dyeing is necessary, because otherwise the tannin will dissolve out and pass into the dyebath during the dyeing, partially precipitate the dyestuff, and so produce uneven dyeings. So, after the leather has been washed with a solution of soda, it is treated with a precipitant, a solution of a titanium or antimony salt, usually titanium potassium oxalate or potassium antimonyl tartrate, the leather being worked about in this bath during immersion. The tannin is thus precipitated within the leather in an insoluble form, and cannot get out into the dyebath; and the leather is also, of course, mordanted by the same process.

The usual precaution of addition of a little acetic acid to the bath is necessary when hard water is used. An impression prevails in some quarters that the use of acid dyestuffs is harmful to the leather, because of the concurrent necessity of using some acid in the bath; but this fear is only partially justifiable; it has a bearing only upon certain special cases. Difficulties arise only when sulphuric acid is the acid used, and when the leather has been tanned with a vegetable tanning-agent; and then, only when the acid is not afterward neutralized. But, when formic acid is used, no difficulties at all occur.

Leather tanned with chromium compounds offers no difficulty in dyeing when the proper routine is followed. After tanning, any acid reaction is neutralized, an after-tanning with sumac or gambier, for the levelling up of the surface-condition, is carried out, then the washing, then a treatment with a mordanting-precipitating bath of an antimony or titanium salt, and then a good washing. Then, before dyeing, the fell is best treated in the customary way to get back into it the proper amount of oil or fat. Such leather is dyed with acid or substantive, or with basic or with alizarine dyestuffs; perhaps, as to relative extent, in that order. Where an addition of an acid is necessary for the proper course of the dyeing, the acid is best not added at first, but only after the dyeing has gone on for awhile.

For 100 kilos of material, the bath may be of 40-50 liters of water, 50-100 ccs. of concentrated ammonia water, then the dyestuff solution mixed with 500-700 ccs. of sumac extract of about 25°B., which has first been diluted with 10/1 volumes of water. As to the dyestuff, its amount varies according to the shade desired, but rarely exceeds 2% of the weight of the material. The fells are first placed one by one in the plumper, and plumped for 15-20 minutes. During the plumping, the concentrated sulphuric acid is diluted with 10 liters of water and added, the plumping being then continued for 15-30 minutes longer. If one is working with substantive dyestuffs only, the use of sulphuric acid and ammonia is not necessary; but it is advisable to add, toward the end of the dyeing, 50-70 ccs. of 30% acetic acid per 100 kilos of fells. After the plumping in dilute sulphuric acid, the acid must be removed, by washing and by final neutralization of the residue, by a rinse in a bath of sodium acetate (for 100 kilos of fells, 250 g. of crystallized sodium acetate). The dyeing is carried out at 50°-60° C. If the chromed leather is to be dyed completely through, such acid dyestuffs as possess a high penetrative power must be used; more ammonia than usual must be added, and the dyeing continued until examination of a fell cut across shows the desired penetration. Sometimes the dyeing with acid dyestuffs is followed by top-dyeing with basics. The oiling can be carried out, finally, without any danger of loss of such a basic dyeing from any solvent action of the fat or oil,

since the acid dyestuff already present in the leather acts to a certain extent as a mordant for the basic dyestuff afterward applied.

With chamois leather, which is more rarely dyed than other kinds, either suitable natural dyestuffs, or a preparation such as Epidermol, with acid or substantive dyestuffs, are used; often such a dyeing is finished by after-dyeing with a basic dyestuff. When dyeings fast to rubbing or washing are required, the alizarine or the sulphur dyestuffs are used. With this kind of leather, all traces of oil, fat, acids, or alkalies must be absolutely removed. Dyeings are frequently made still more fast by after-chroming.

In general, leather dyeing does not differ from the dyeing, say, of wool, except for modifications which would be obviously necessary in dealing with a material which is in thick sheets instead of fine fibers, which is therefore not nearly so permeable to solutions, which through its pretreatment is more or less irregularly prepared, and which through its lower permeability is likely to contain more than traces, irregularly distributed, of the chemicals used in its preparation.

Brown Dyestuffs for Wool

German Patent No. 455,033 (5/I/'28)—*I. G. Farben-Ind. A.G.*—Two mols of 4-nitro-1-chlorbenzene-2-sulphonic acid are condensed, in the presence of acid-neutralizing agents, with one mol of a 1-3- or 1-4-diamino-compound of the benzene series. The product is reduced on the two nitro-groups, and these two amino groups are similarly substituted, in the presence of neutralizing compounds, with dinitro-halogen derivatives of the benzene series. Two examples are given, of dyestuffs dyeing wool in yellow-brown to brown tones, of great fastness.

Chrome Eczema

W. E. Englehardt and R. L. Mayer Arch.—fur Gewerbepath und Gewerbehyg 931, 2, 140, 168 *Through U. S. D. C.*

The incidence of chrome eczema amongst working people coming in contact with chromium compounds has been investigated. Subsequent tests with 0.5% bichromate solution indicate that 74% of cases of chrome eczema are due to personal idiosyncrasies which may either be inherent or induced by contact. The importance of wearing rubber gloves to protect the forearms, and thorough washing of arms is indicated. The frequent use of sodium bisulphite solution to reduce the injurious action is regarded as essential.

Dry-Cleaning and Wet-Washing of Acetate Silk

O. Braun—Deutscher Faerber-Ztg. 67, 136 (1931).—As characteristically differing in chemical and physical properties from all the other types of natural or artificial fibers, acetate silk must be handled with due regard to these special properties, if the goods are not to suffer in either luster or tensile strength. Contrary to some impressions which still prevail, here and there, acetate silk is decidedly resistent toward the action of many common and cheap dry-cleansing agents. Also, many of the special dyestuffs now used for the dyeing of acetate silk are resistent toward such cleansing agents, which was not the case not so many years ago, when the commoner dyestuffs, in use and satisfactory for other fibers, were giving acetate silk a bad reputation. Gasoline and other liquids of the same sort, hydrocarbon mixtures of the paraffine and benzene series—benzene, toluene, xylene, are good, as well as the more common and in many ways more desirable carbon tetrachloride. Of course, all such solvents should be used cold.

Care has to be exercised, however, with some of the solvents which have proved themselves very valuable with other fibers. Acetone, chloroform, tetrachlorethane, etc., attack acetate silk very vigorously, speedily swelling and actually dissolving the fiber, and so hopelessly ruining the weave.

In wet-washing, there are certain points which must be kept in mind to insure the goods coming out unharmed.

a.—The presence of acetate silk in the weave, whether the goods be a mixed or single-component weave, must be recognized, and such goods should be plainly marked as such, for the guidance of the worker, by some means, as attachment of an indelible label, woven or otherwise.

b.—When acetate silk is present in the goods, the water or soap-baths employed must not exceed 75°C. Over this temperature, saponification of the acetate sets in, however slowly according to circumstances; and the luster of the acetate silk is in danger of suffering. When the goods are treated in the manner customary for natural silk or wool, where the lower range of temperatures prevails, there is no danger of saponification.

c.—Acetate silk is very stable toward acids, such as are found in perspiration, at least, but any alkalies of any decided strength damage it at once (by saponification). Ammonia is not harmful, and soda can be safely employed up to a concentration of 7-8 g. per 5 liters in the wash-fluids; but not more.

d.—Except for weaves of strongly-twisted acetate silk yarn, acetate silk goods should not be worked in machines with unpolished working surfaces, or in machinery in which the goods are pressed or squeezed; e.g., in rotary washing-machines. Fine, or soft, loose weaves should be treated in open vessels, by hand as far as possible, as is done for similar tender weaves, as natural silk, etc. In this way the sharp, persistent creases, which it is impossible to get rid of, and which always result from rough mechanical handling, are avoided.

e.—The delicate luster of acetate silk, so similar to that of natural silk, and one of the fiber's most valuable properties, is easily altered by ironing at too high a temperature, to a more decidedly glossy luster, which is not at all desirable. If the ironing is carried out at an unreasonably high temperature, the fiber will become brit-

(Continued on page 551)

A New Colorimetric Test for Chromium*

By **G. C. SPENCER**

Bureau of Chemistry and Soils, Washington, D. C.

—During the past two or three years there has been considerable interest in the establishment of the best methods for determining minute quantities of metals in textile fabrics. A sub-committee of the A. A. T. C. C. has been working along this line and their most recent report is published in the 1931 Year Book of the Association. It was thought that the present article describing a new colorimetric test for chromium textile materials would be of interest to the readers of the Dyestuff Reporter, and for this reason it is being published as a reprint.—

WHILE searching for methods of determining minute quantities of chromium, the writer recalled a dyeing technic in which woolen fiber colored with certain acid dyestuffs is given a subsequent treatment in a bath containing potassium dichromate and sulphuric acid. In many cases this after-chroming effects a distinct color change on the woolen fabric and greatly increases the fastness of the color.

This technic suggested a possible method for the detection of small quantities of chromium by warming previously dyed wool samples in acid solutions that were known or believed to contain chromic acid. Preliminary experiments were accordingly made on woolen yarn that had been dyed with 1 per cent of serichrome blue R[1, 2] with results which justified further experimentation. This dyestuff, serichrome blue R, despite its name, imparts to wool a bright crimson color with a faint bluish tinge. The deep navy blue shade of the finished wool is developed by chromic acid in the second bath. No other dyestuff seemed to offer any advantages over this for analytical purposes. It is possible that some other dye would be better for quantitative results.

For this work wool flock (finely ground wool) was used, although woolen yarn may be used if preferred. The dyestuff solution was made by dissolving 100 mg. of serichrome blue R in water and making up to 200 cc.

The dyeing operations used were the following:

To a 125-cc. Erlenmeyer flask were added 40 cc. of water, 0.1 gram of sodium sulphate, and 0.02 gram of sulphuric acid. (The quantities of sodium sulphate and sulphuric acid added represent 5 per cent and 1 per cent, respectively, of the weight of the wool taken.) Two grams of the wool were added and the flask was shaken to ensure thorough wetting of the fiber. The desired quantity of dyestuff was then added (0.5 per cent is recommended—i.e., 20 cc. of the solution). The mixture was stirred well and heated at full temperature of the steam bath for 30 minutes, after which it was filtered on paper by suction in a Büchner funnel, washed free of acid, and dried.

The color standards were prepared as follows: A standard chromium solution was made by dissolving 0.282 gram of potassium dichromate in water and making up to a volume of 100 cc. (1 cc. of this solution contains 1 mg. of chromium as Cr.) From this solution a working standard containing 0.01 mg. of chromium in each cubic centimeter was made.

To each of ten beakers were added 50 cc. of water, 3 cc. of 1 *N* sulphuric acid (not standardized), and 0.1 gram of wool previously dyed with serichrome blue R. The mixture was stirred to ensure thorough wetting of the fiber and such quantities of the potassium dichromate solution as represented from 0.01 mg. to 0.1 mg. of chromium were added to the respective beakers, which were then covered with watch glasses. The mixture was heated on a steam bath at full temperature from 20 to 30 minutes with occasional stirring, filtered by suction on paper (small Büchner), washed, dried, and mounted on a spot plate in Duco household cement thinned down with an equal quantity of amyl acetate. The wool samples thus treated were found to have developed a blue shade in proportion to the amount of chromium which acted on the dyed sample.

To test for chromium in unknown samples, separate the chromium, ferric iron, and aluminum in the form of hydroxides. Filter by suction in a Gooch crucible provided with an asbestos mat (preferably on a removable disk) and wash with water. Remove the asbestos with the precipitate to a beaker and add 30 cc. of water and 3 cc. of normal sodium hydroxide solution. Mix well and add 5 cc. of hydrogen peroxide solution (U. S. P.). Allow to stand about 30 minutes, and then warm on a steam bath until hydrogen peroxide is decomposed. Filter by suction and acidify the filtrate with 3 cc. excess of normal sulphuric acid, add with stirring 0.1 gram of dyed wool, and heat the covered beaker on the steam bath from 20 to 30 minutes. Filter by suction on paper, wash, and dry.

The presence of chromium is indicated by the development of a blue shade on the red fiber. If this color is not too dark the quantity of chromium may be estimated by comparison with the chromium color standards described above.

Confirmation of the method as here presented was made by comparing the colors developed by potassium dichromate solutions with those produced by chromic chloride solutions after oxidation. Both solutions, potas-

*Ind & Eng. Chem.

sium dichromate and chromic chloride (solution A), were adjusted to contain 0.01 mg. of chromium in 1 cc. The first color standards represented 0.05, 0.07, 0.10, and 0.12 mg. of chromium, respectively, besides a blank. In the first case chromic chloride alone was used, in the second cast the chromium solutions contained an admixture of ferric alum and alum. Fair duplication of solution A colors with those made by potassium dichromate was observed in all cases. More complete tests were then made using solution A in amounts that varied from 0.01 to 0.10 mg. of chromium, with checks that were invariably satisfactory. These results confirmed a number of tests that were obtained in earlier experiments in which potassium permanganate was used as an oxidizing agent instead of hydrogen peroxide.

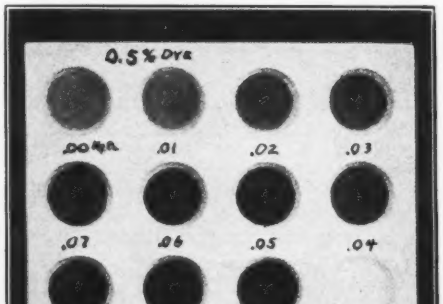

Fig. 1

Photographs of these chromium blue developments are readily distinguished from one another, as may be observed in Figure 1. In making these photographs the range of chromium color distinctions was materially extended by the use of light screens.

It is also of interest to note that chromium-developed wool samples may be stripped of their red color by warming with dilute alkali solution (0.1 *N* sodium carbonate) without removing the chromium stain. These stains are proportional to the quantity of chromium present.

In order to ascertain if the color development herein described is characteristic of chromic acid, parallel experiments were tried on woolen yarn dyed with serichrome blue R using the following acids and salts in amount equivalent to 1 mg. of metallic chromium: molybdic, tungstic, vanadic, and permanganic acids; also ferrous sulphate, manganous sulphate, and chrome alum. No change in color was observed.

Literature Cited

[1] Friedlander, V., *Fortschr. Theerfarbenfabrikation ver. Ind.*, *3*, 791-3 (1896).

[2] Schultz, G., Farbstofftabellen (1914) Dye No. 164.

Contribution 127 of Food Research Division, Bureau of Chemistry and Soils.

Technical Notes from Foreign Sources

(Continued from page 549)

tle, and assume a roughness of surface very perceptible to the touch.

Since acetate silk retains much less moisture, after washing, than do the other fibers, it can be ironed at a lower temperature than is customary, thus avoiding any danger of damage by heat. The use of a little beeswax on the iron is advisable, as the smoothness thereby gained prevents any sticking of the iron, and so the partial fusion of the fiber, which is what brings about the brittleness of fiber and strong alteration of luster above mentioned.

Standardization of Colors

B. Teufer—Kunst-Seide 14, 15 (1932).—A discussion of the principles and ideals involved in the problem.

Some aspects of the purpose of standardization are obvious. The first purpose in any case is simplification of processes and lowering of costs, by selecting for the standards such products, or such dimensions in which the products are turned out, as can in a practical way be furnished to the consumer most easily. It is not always kept in mind, however, that other products, or other sizes of product, should always be thought of as needing to be producible upon demand for a special need, though at a higher cost and with some possible delay. In the establishment of standards, it is true that some of the norms established can perfectly well be looked upon as probably valid for an unlimited time (cf. the metric system, in measurements); but, in general, it may also be kept in mind that, for sufficient reasons coming into operation or discovered after establishment of the standards, such established standards can easily be modified or completely abolished, or simply extended further, if and when such action proves necessary. Standardization may extend to the most varied elementary details; for example, the fixing of concepts, unification of characteristic details and the mental impression thereby normally produced, establishment of units for measurement of distances, surfaces, spaces, weights, the establishment of serially definite color-tone scales, the choice of sizes from a large series of possible sizes (this has already been done, e.g., in mechanics; cf. standard screw-threads), limits of allowable variations in size (automobile engine parts, etc.), standard methods of testing (mechanics and chemistry), and so on.

To be laid down as fundamental are the following principles:

1.—A progressive sequence of steps in the field under consideration must be possible, whether a sequence of dimension or of quality.

2.—There must be a clear conception of the characteristic designation of the norm-object. Simple, definite, and generally comprehensible designations must be available, or, if not already in existence, must be devised.

3.—A standardization cannot be established, if quantity or quality are not mensurable (e.g., the relative strengths

of odors or perfumes cannot be reduced to numerical values), for in that case all means of recognition, and all possibility of adjustment and comparison are lacking.

Now, in the standardization of colors, these fundamental rules of course apply. Not so many years ago we had no systematic scale or concepts whatever; but Ostwald's work has provided a color-scale, an exact method of color-designation, and a method of color analysis, which are easily comprehended, and appear to be practically usable. Other schemes have of course been proposed, and it also is not denied that the Ostwald method may have its disadvantages or even errors (it is not hinted that such is the case, it is merely not denied that the possibility may exist, and that such defects may come to light as the method is more widely practiced); but the point emphasized is, that in it we have at least a working method of a very definite and fairly simple sort. Such a working method being provided, it becomes necessary to sort out the almost unlimited number of known color tones into a series of desirable standards differing from each other by uniform steps, the precise number of recognizable unit-differences being of not much importance, provided that the interval between each step is precisely determined. It has, up to the present, proved possible to construct such a series of standards which will meet with general approval. There are in existence many sets of standards, which could easily be duplicated, worked out by chemists and dyers in connection with the products of particular dyestuff manufacturers; such color cards are of great use within their limits, but cannot, till correlated and reduced, serve as general standards, so much to be desired.

New du Pont Dye

Pontamine Diazo Blue 6G is a new dyestuff developed by the Dyestuffs Division of E. I. du Pont de Nemours & Company. It is a direct color recommended by du Pont for development with beta naphthol.

The dyestuff is said to be of greatest value for discharge purposes, giving clear whites on cotton and tinted whites on silk. The general fastness of this color is claimed to be sufficiently good to meet all ordinary requirements for women's dress-goods and similar fabrics.

It is stated that this dyestuff will be most widely used on cotton and rayon but may also be applied to pure silk when dyed in an acid bath.

Swiss Dye Exports in 1932 Concentrated in Europe

Swiss exports of dyes during the first half of 1932 fell below the level of the 1931 period, 3,196,399 kilos of coal-tar dyes valued at 29,727,306 Swiss francs being shipped in 1932 six months' period compared to 3,821,858 kilos worth 32,063,887 Swiss francs in the 1931 six months. Almost all of the 1932 Swiss exports were consumed in Europe, countries in this area accounting for 2,376,295 kilos, while Asia and North America were the destination of 380,249 kilos and 308,027 kilos, respectively. (Value of Swiss franc 1931—$0.1940; six months 1932—$0.1947.)

NEW PATENTS

Abstracted by Synthetic Organic Chemical Mfrs. Association.

Anthraquinonyl-Amino Derivatives of Benzanthrone-pyrazolanthrone. (Gray to blue vat dyestuffs.) Max Albert Kunz, of Mannheim, and Karl Koeberle of Ludwigshafen-on-the-Rhine, Ger., assignors to General Aniline Wks., Inc., of N. Y., N. Y., No. 1.857,553, May 10, 1932.

Metal Compounds of Azo-Dyestuffs and Process of Making Same. (Dye vegetable fiber and especially artificial silk from so-called regenerated cellulose grey, green-grey to blue-grey tints.) Fritz Straub and Walter Anderau, of Basel, Switzerland, assignors to the firm "Society of Chemical Industry in Basle," of Basel, Switzerland, No. 1,857,572, May 10, 1932.

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

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EXPERIENCED SALESMAN - DEMONSTRATOR, Chicago Territory. Has thorough knowledge of all dyestuffs, imported as well as domestic, their application, and the use of all finishing materials, water softeners, penetrators, etc. Practical Dyehouse experience. References. Address Box No. 740, American Dyestuff Reporter, 440 Fourth Avenue, New York.

DYER—of Cotton and Rayon, Piece Goods. Many years experience. Specialized in Vats, Naphthols and Developed Colors, for Solid or Discharge Work. Any style fabric; also direct and Sulphur Colors, Pads, Jiggs and continuous machines. Very good knowledge of chemistry and starching. Address Box No. 743, American Dyestuff Reporter, 440 Fourth Avenue, New York.

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